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(54) Titre : PARTICULES COMPRENANT UN SILOXANE FLUORE ET PROCEDES DE FABRICATION ET D'UTILISATION DE CELLES-CI
 (54) Title: PARTICLES COMPRISING A FLUORINATED SILOXANE AND METHODS OF MAKING AND USING THE SAME

(57) **Abrégé/Abstract:**

Particles, including proppants, comprising a fluorinated siloxane. The particles are useful as proppants in fractured a subterranean geological formation comprising hydrocarbons.

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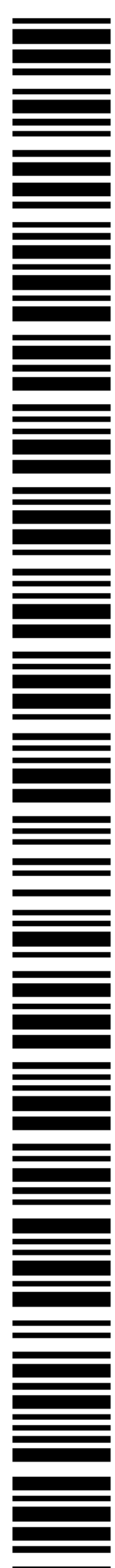
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(54) Title: PARTICLES COMPRISING A FLUORINATED SILOXANE AND METHODS OF MAKING AND USING THE SAME

(57) Abstract: Particles, including proppants, comprising a fluorinated siloxane. The particles are useful as proppants in fractured a subterranean geological formation comprising hydrocarbons.



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**PARTICLES COMPRISING A FLUORINATED SILOXANE
AND METHODS OF MAKING AND USING THE SAME**

Background

5 [001] Oil and natural gas can be produced from wells having porous and permeable
subterranean formations. The porosity of the formation permits the formation to store oil
and gas, and the permeability of the formation permits the oil or gas fluid to move through
the formation. Permeability of the formation is essential to permit oil and gas to flow to a
location where it can be pumped from the well. Sometimes the permeability of the
10 formation holding the gas or oil is insufficient for the desired recovery of oil and gas. In
other cases, during operation of the well, the permeability of the formation drops to the
extent that further recovery becomes uneconomical. In such cases, it is common to
fracture the formation and prop the fracture in an open condition using a proppant material
or propping agent. Such fracturing is usually accomplished by hydraulic pressure. The
15 proppant material or propping agent is typically a particulate material, such as sand and
(man-made) engineered proppants, such as resin coated sand and high-strength ceramic
materials (e.g., sintered bauxite, crystalline ceramic bubbles, and ceramic (e.g., glass)
beads), which are carried into the fracture by a fluid.

[002] Further, for example, if relatively light weight, porous crystalline ceramic (e.g.,
20 alumina) proppants are used, fluid (e.g., the fracturing fluid) can penetrate into the
proppant increasing its density, which can in turn can adversely affect the flow of the
proppant into the fractured areas.

[003] There continues to be a need for additional proppant options, preferably, proppants
with improved properties. Also, for example, there is a desire, particularly for relatively
25 light weight, porous proppants, to prevent, or at least reduce, penetration of fluids into the
proppants.

Summary

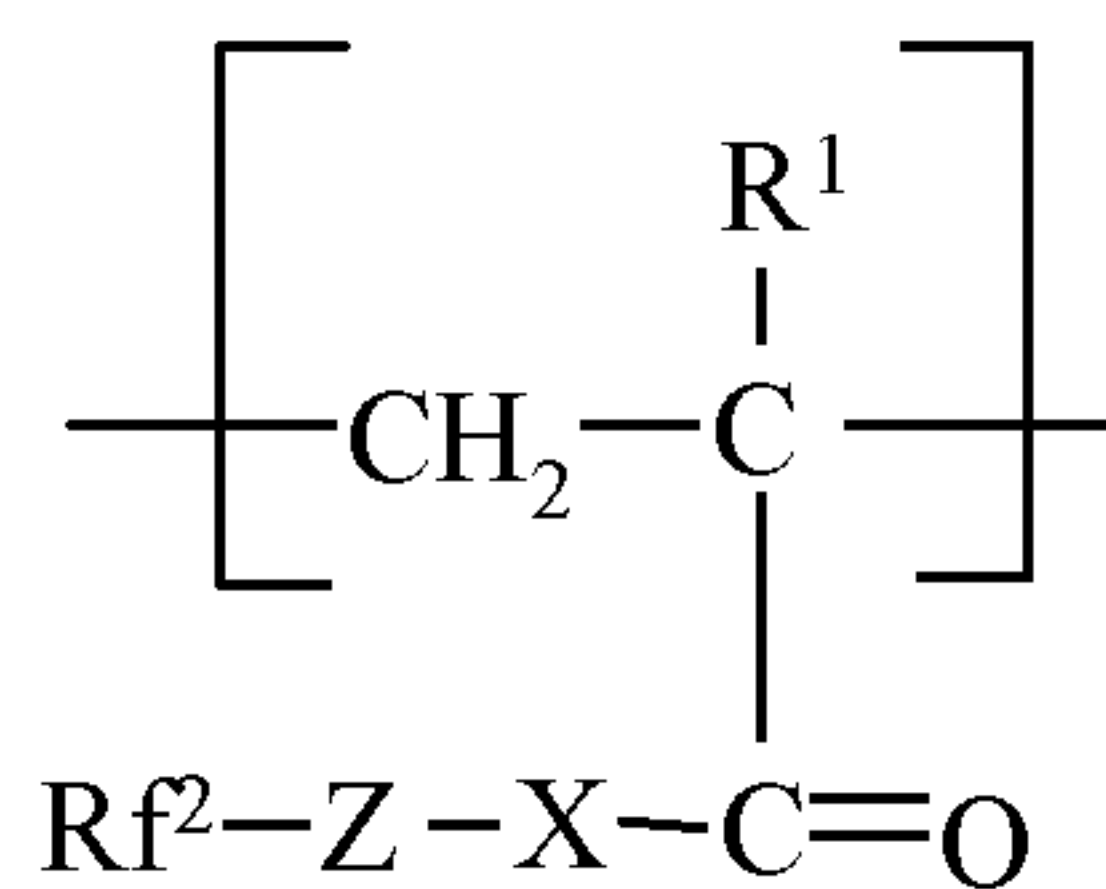
[004] In one aspect, the present invention provides particle(s) treated with at least one
30 fluorinated siloxane, the particle being at least 500 micrometers (in some embodiments, at
least 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, or even at least 1700

micrometers; in some embodiments, in a range from 500 micrometers to 1700 micrometers) in size, wherein , wherein the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from the group consisting of:



5 a polymeric fluorinated composition comprising:

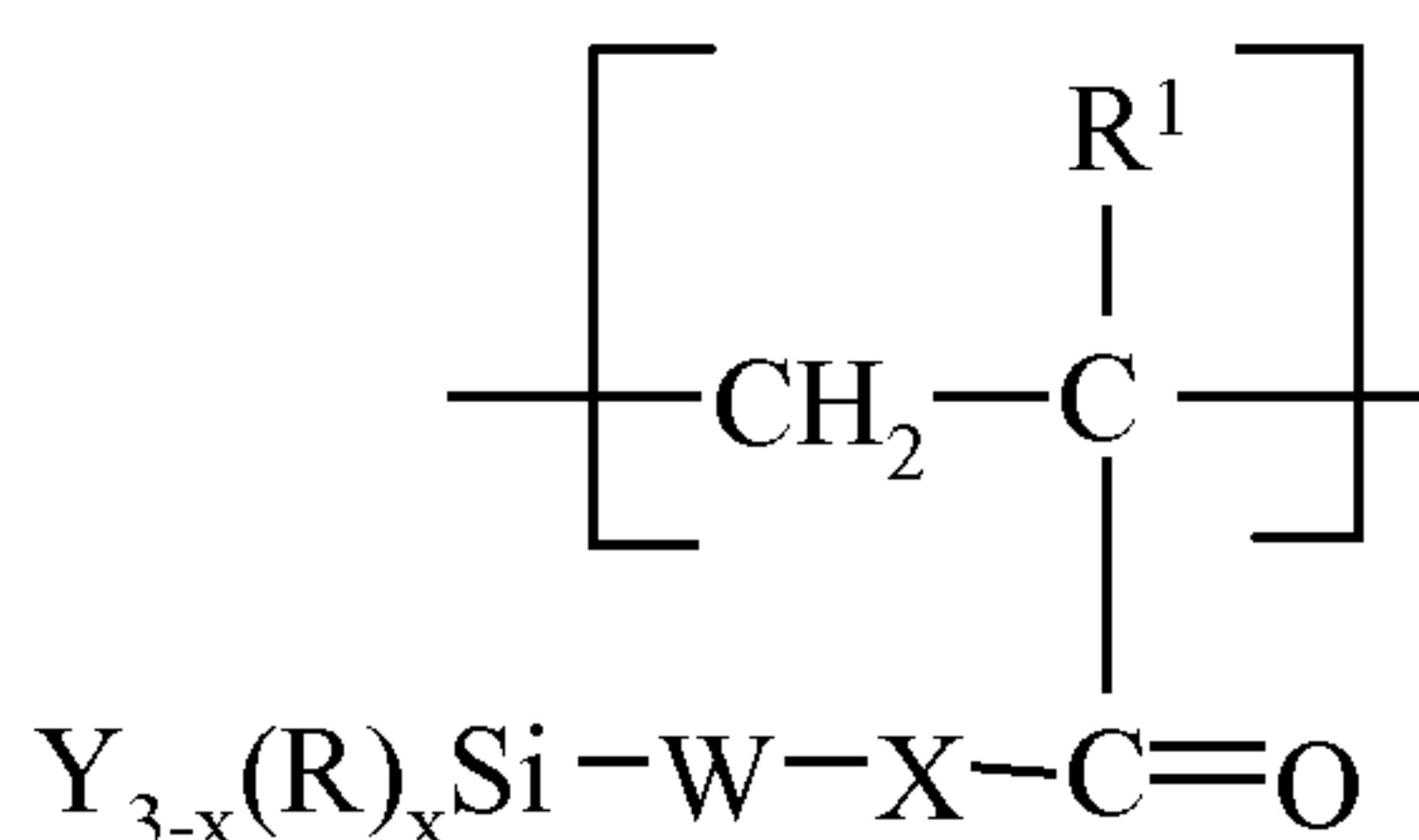
at least one divalent unit represented by the formula:



and

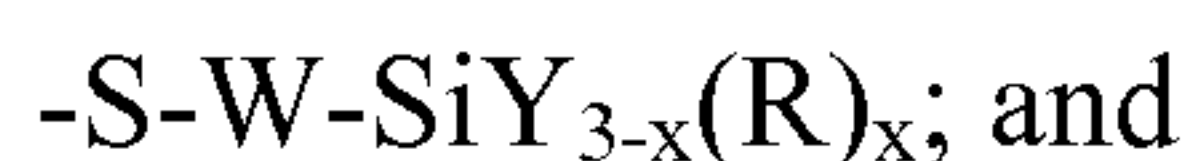
at least one of

at least one divalent unit represented by the formula:



or

a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

15 at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one $-\text{O}-$;

Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one $-\text{O}-$;

20 each R is independently selected from the group consisting of alkyl having one to six carbon atoms and aryl;

Q is a divalent or trivalent organic linking group;

each Y is independently selected from the group consisting of hydroxyl, alkoxy, acyloxy, and halogen;

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each R¹ is independently selected from the group consisting of hydrogen and alkyl having one to four carbon atoms;

each W is independently selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently selected from the group consisting of -NH-, -O-, and -S-;

X¹ is selected from the group consisting of -NH-, -S-, -O-, -O-C(O)-NH-, and -O-alkylene-O-C(O)-NH-;

Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

z is 1, 2, 3, or 4.

In some embodiments, the treated particles are included with a plurality of other particles (i.e., a plurality of particles comprising the treated particles having the specified size). In

some embodiments, the "other particles" may be or include "treated particles" less than 500 micrometers in size. In some embodiments, these particles collectively have particles in a range from 100 micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh (ANSI)) (in some embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000 micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850 micrometers (i.e., about 40 to about 20 mesh), or 300 micrometers to 600 micrometers (i.e., about 50 mesh to about 30 mesh). In some embodiments, the "collective" plurality of particles comprises at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even at least 100 percent by weight of the treated particles. In some embodiments, the fluorinated siloxane is bonded to the treated particle. In some embodiments, the particle is made of a material selected from the group consisting of said, thermoplastic, clay, glass and alumina.

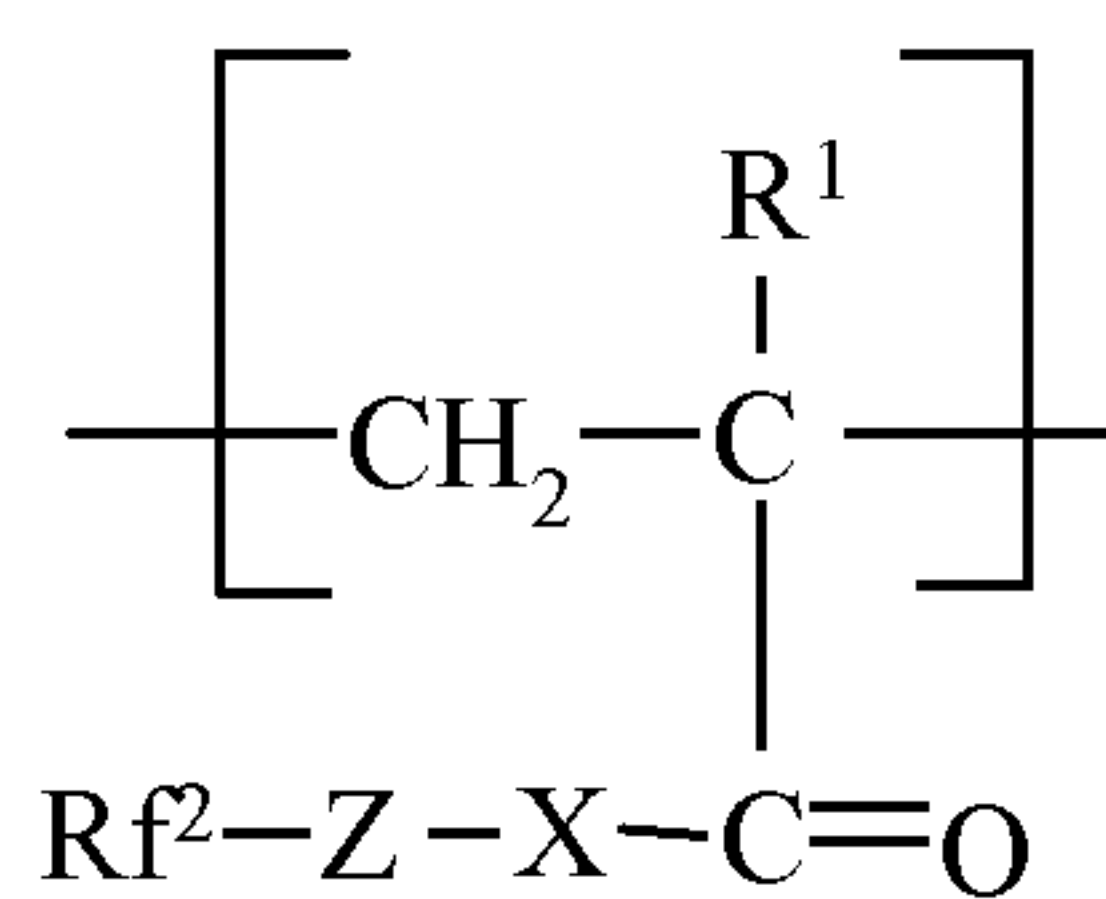
[005] In another aspect, the present invention provides a ceramic (i.e., glass, crystalline ceramic, glass-ceramic, and/or combinations thereof) particle comprising at least one fluorinated siloxane, wherein the ceramic particle has a plurality of pores, and , wherein

the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from the group consisting of:



a polymeric fluorinated composition comprising:

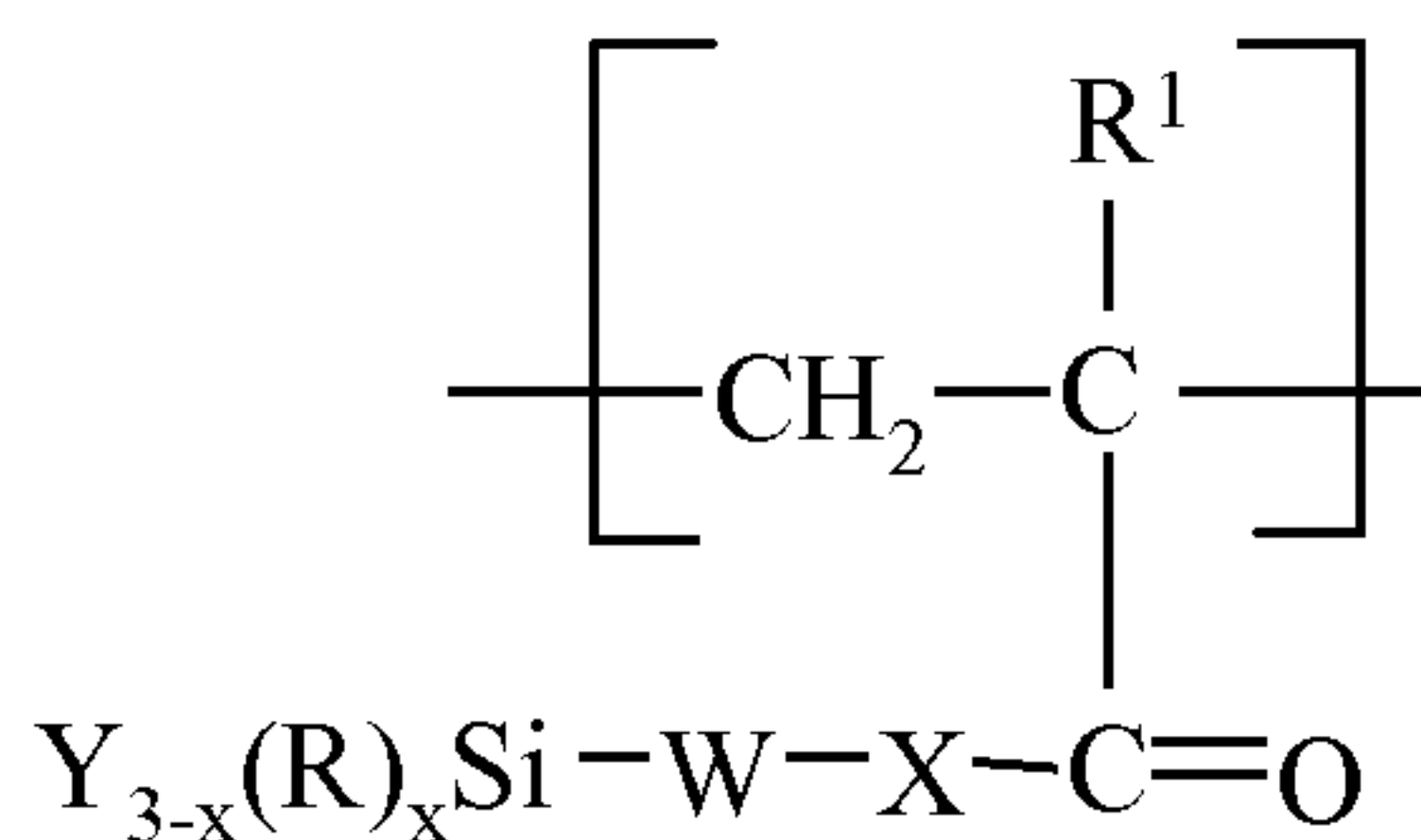
5 at least one divalent unit represented by the formula:



and

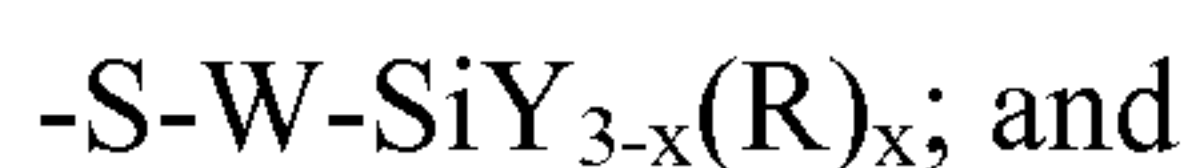
at least one of

at least one divalent unit represented by the formula:



or

10 a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

15 wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-;

Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

20 each R is independently selected from the group consisting of alkyl having one to six carbon atoms and aryl;

Q is a divalent or trivalent organic linking group;

each Y is independently selected from the group consisting of hydroxyl, alkoxy, acyloxy, and halogen;

25 each R¹ is independently selected from the group consisting of hydrogen and alkyl having one to four carbon atoms;

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each W is independently selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently selected from the group consisting of -NH-, -O-, and -S-;

5 X¹ is selected from the group consisting of -NH-, -S-, -O-, -O-C(O)-NH-, and -O-alkylene-O-C(O)-NH-;

Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

10 z is 1, 2, 3, or 4.

The pores can be closed or open with respect to each other, or a mixture of opened and closed porosity. In some embodiments, the ceramic particles have a density of at least 2 g/cm³ (in some embodiments, at least 2.5 g/cm³, at least 3 g/cm³; in some embodiments, in a range from 2 g/cm³ to 3 g/cm³). In some embodiments, the treated particles are included with a plurality of other particles (i.e., a plurality of particles comprising the specified treated particles). In some embodiments, the particles are treated with at least one fluorinated siloxane precursor during injection into the fracture, wherein the fluorinated siloxane precursor is converted to the fluorinated siloxane. In some embodiments of the present invention, the fluorinated siloxane is bonded to the particles. In some 20 embodiments, the particles are at least 100 micrometers (in some embodiments, at least 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2500, or even at least 3000 micrometers; in some embodiments, in a range from 500 micrometers to 1700 micrometers) in size. In some embodiments, the treated particles have particle sizes in a range from 100 micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000 micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers (i.e., about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60 mesh to about 40 mesh), 200

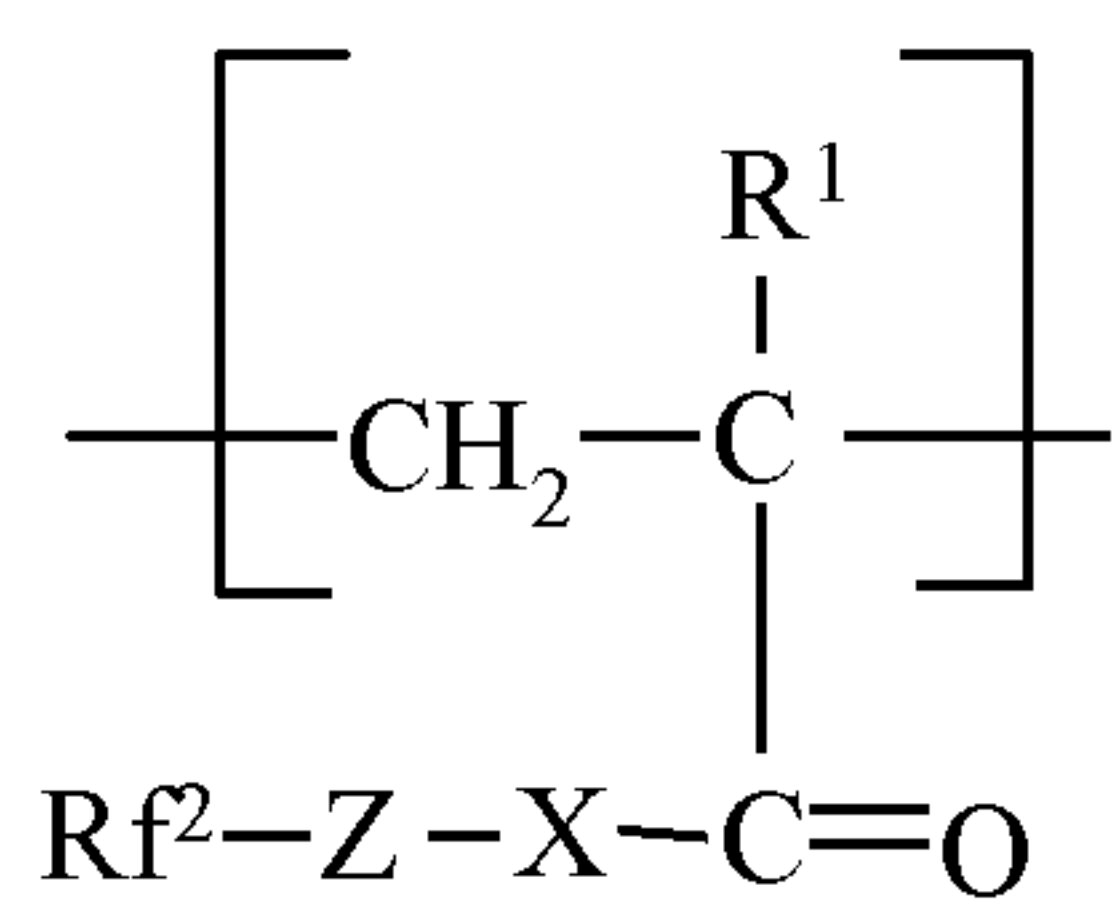
micrometers to 425 micrometers (i.e., about 70 mesh to about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70 mesh). In some embodiments, the treated particles are included with a plurality of other particles (i.e., a plurality of particles comprising the treated particles). In some embodiments, these particles collectively have particles in a range from 100 micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000 micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers (i.e., about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60 mesh to about 40 mesh), 200 micrometers to 425 micrometers (i.e., about 70 mesh to about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70 mesh). In some embodiments, the “collective” plurality of particles comprises at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even at least 100 percent by weight of the treated particles.

[006] In another aspect, the present invention provides an engineered proppant comprising at least one fluorinated siloxane comprising a condensation product of at least one reactive fluorinated silane selected from the group consisting of:



a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula:

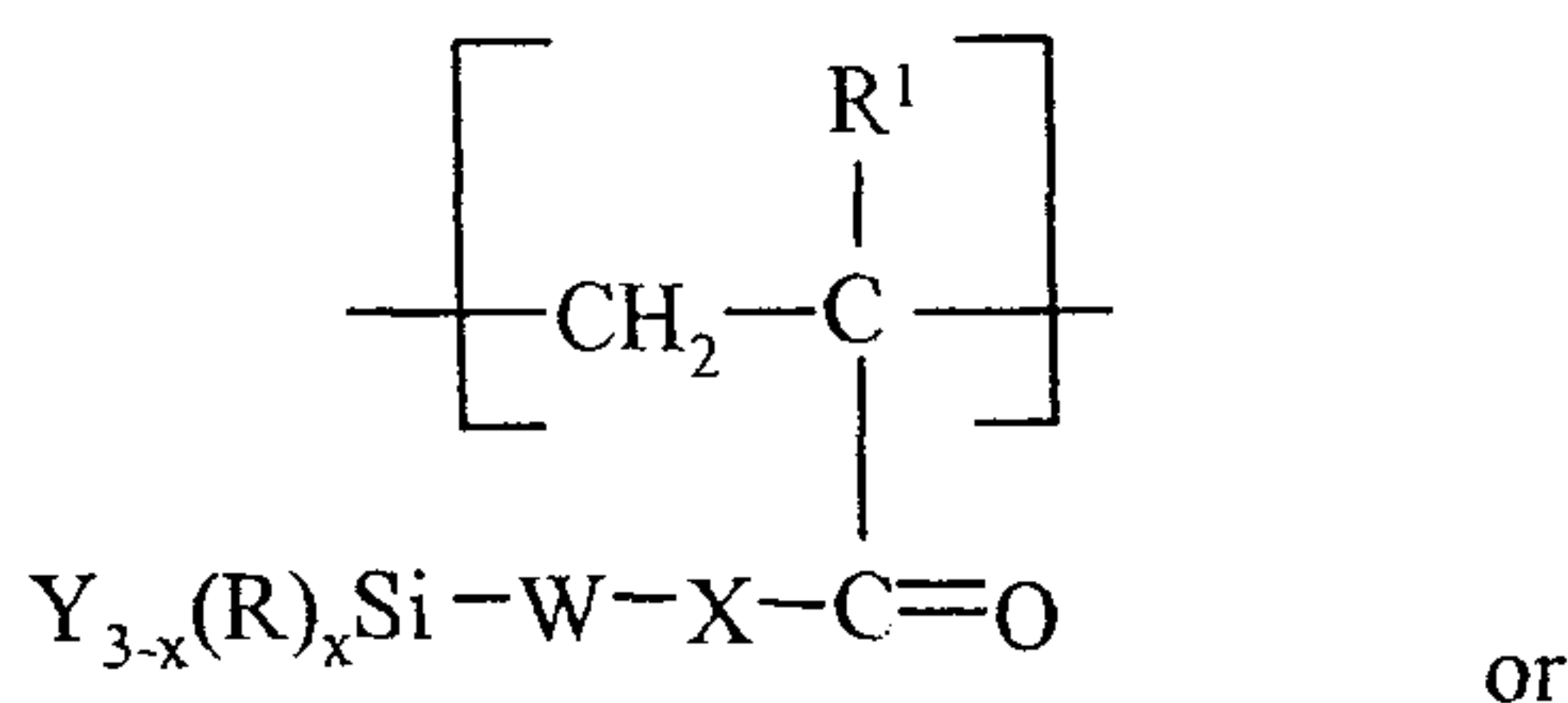


and

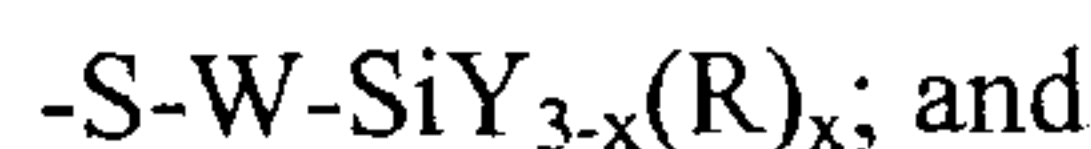
at least one of

at least one divalent unit represented by the formula:

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a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

- 5 at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and
 at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one $-\text{O}-$;

- 10 Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one $-\text{O}-$;
 each R is independently selected from the group consisting of alkyl having one to six carbon atoms and aryl;

Q is a divalent or trivalent organic linking group;

- 15 each Y is independently selected from the group consisting of hydroxyl, alkoxy, acyloxy, and halogen;

 each R¹ is independently selected from the group consisting of hydrogen and alkyl having one to four carbon atoms;

- 20 each W is independently selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

 each X is independently selected from the group consisting of $-\text{NH}-$, $-\text{O}-$, and $-\text{S}-$;

 X¹ is selected from the group consisting of $-\text{NH}-$, $-\text{S}-$, $-\text{O}-$, $-\text{O}-\text{C}(\text{O})-\text{NH}-$, and $-\text{O}-\text{alkylene}-\text{O}-\text{C}(\text{O})-\text{NH}-$;

Z is a divalent organic linking group;

- 25 x is 0, 1, or 2;
 y is 1 or 2; and
 z is 1, 2, 3, or 4.

In some embodiments, the particles are treated with at least one fluorinated siloxane precursor during injection into the fracture, wherein the fluorinated siloxane precursor is

converted to the fluorinated siloxane. In some embodiments of the present invention, the fluorinated siloxane is bonded to the particles. In some embodiments, the particles are at least 100 micrometers (in some embodiments, at least 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2500, or even at least 3000 micrometers; in some embodiments, in a range from 500 micrometers to 1700 micrometers) in size. In some embodiments, the treated particles have particle sizes in a range from 100 micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000 micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers (i.e., about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60 mesh to about 40 mesh), 200 micrometers to 425 micrometers (i.e., about 70 mesh to about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70 mesh). In some embodiments, the treated particles are included with a plurality of other particles (i.e., a plurality of particles comprising the treated particles). In some embodiments, these particles collectively have particles in a range from 100 micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000 micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers (i.e., about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60 mesh to about 40 mesh), 200 micrometers to 425 micrometers (i.e., about 70 mesh to about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70 mesh). In some embodiments, the “collective” plurality of particles comprises at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even at least 100 percent by weight of the treated particles.

[007] In another aspect, the present invention provides a method of fracturing a subterranean geological formation comprising hydrocarbons, the method comprising:

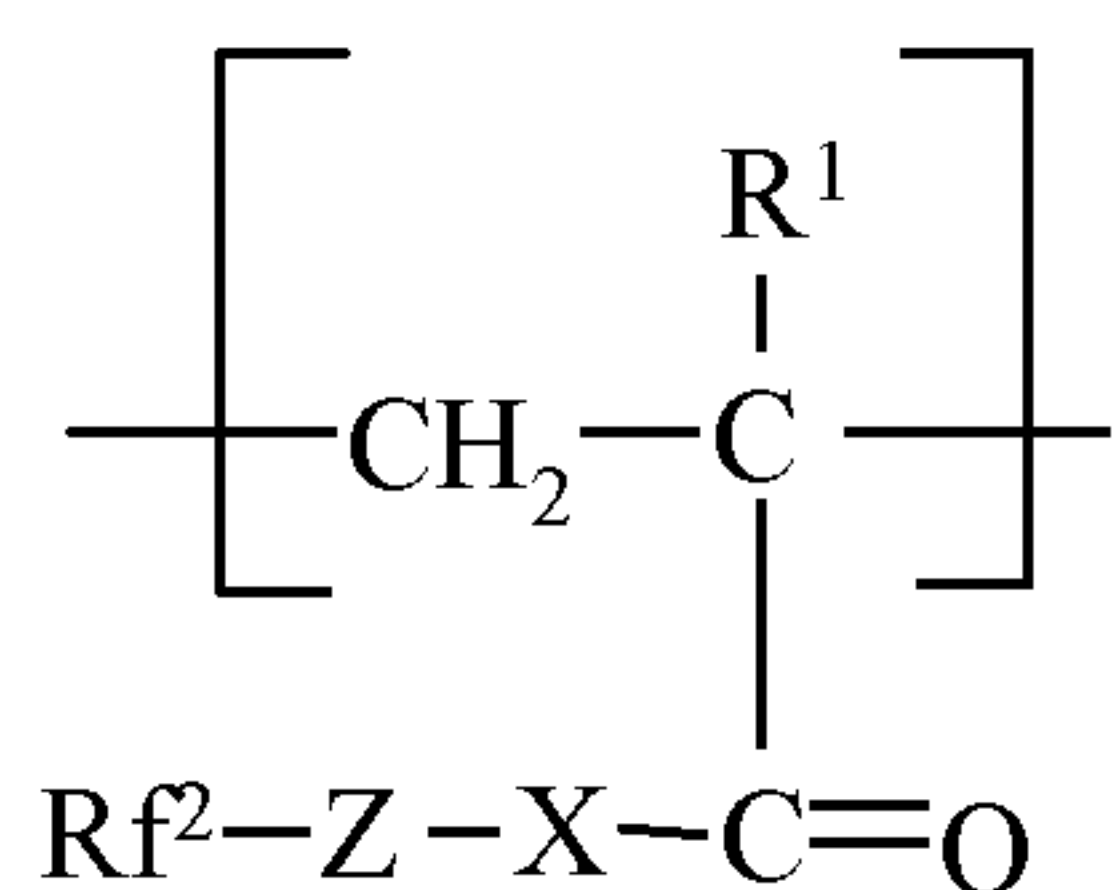
injecting a hydraulic fluid into a subterranean geological formation comprising hydrocarbons at a rate and pressure sufficient to open a fracture therein; and

5 injecting into the fracture a fluid containing a plurality of the particles treated with at least one fluorinated siloxane comprising a condensation product of at least one reactive fluorinated silane selected from the group consisting of:



a polymeric fluorinated composition comprising:

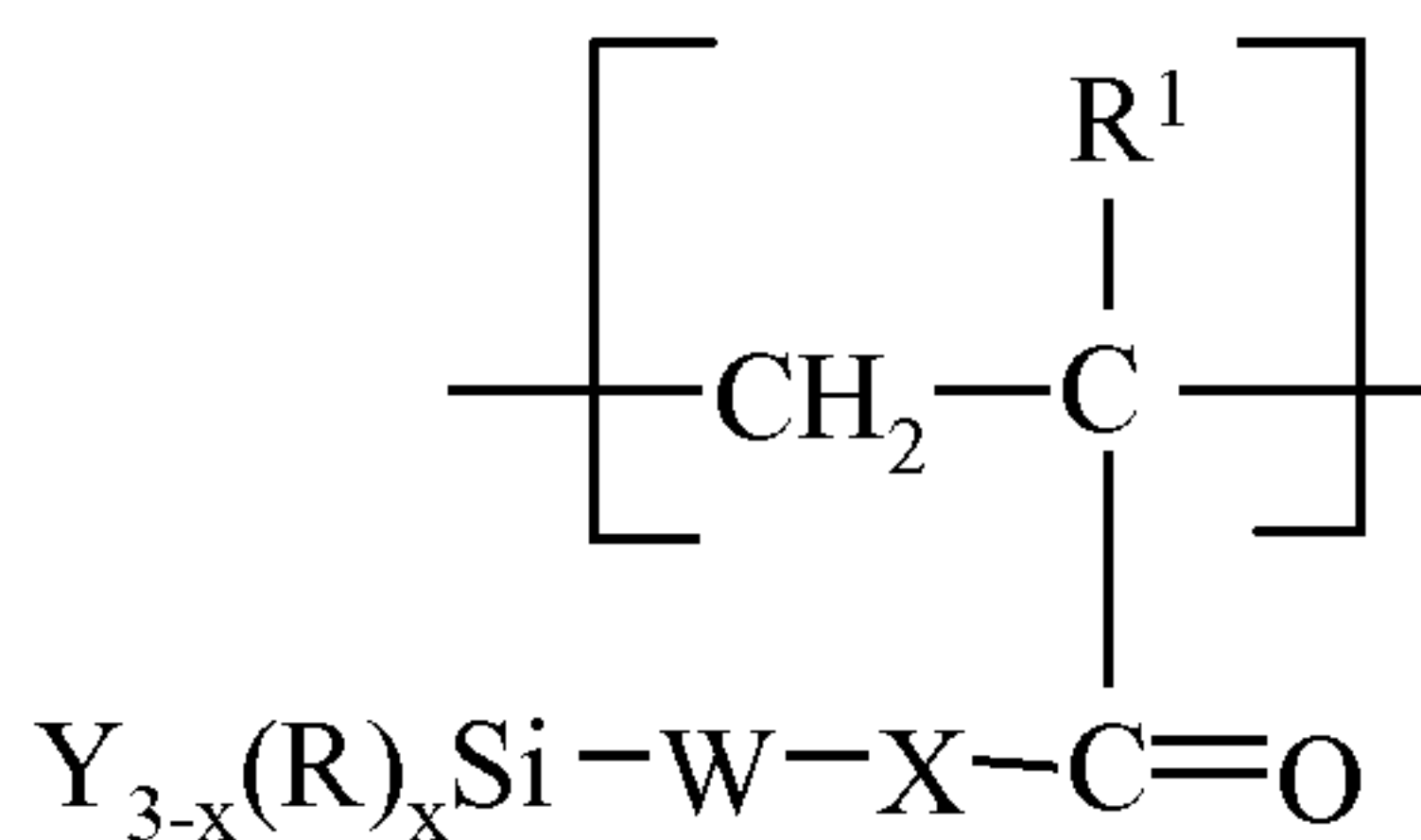
10 at least one divalent unit represented by the formula:



and

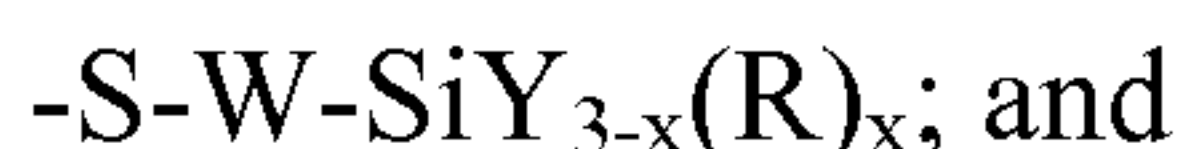
at least one of

at least one divalent unit represented by the formula:



or

15 a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

20 wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-;

Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

25 each R is independently selected from the group consisting of alkyl having one to six carbon atoms and aryl;

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Q is a divalent or trivalent organic linking group;

each Y is independently selected from the group consisting of hydroxyl, alkoxy, acyloxy, and halogen;

5 each R¹ is independently selected from the group consisting of hydrogen and alkyl having one to four carbon atoms;

each W is independently selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently selected from the group consisting of -NH-, -O-, and -S-;

10 X¹ is selected from the group consisting of -NH-, -S-, -O-, -O-C(O)-NH-, and -O-alkylene-O-C(O)-NH-;

Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

15 z is 1, 2, 3, or 4.

In some embodiments, the fracture has a conductivity improved by the presence of the fluorinated siloxane. The conductivity of a fracture is a measure of the effectiveness of a hydraulically treated fracture or essentially how well the fracture improves the flow of oil or gas from the formation. The conductivity of a fracture can be determined using API
20 Conductivity Test RP 61, entitled "Recommended Practices for Evaluating Short Term Proppant Pack Conductivity" (October, 1989).

[008] In some embodiments, the particles (including engineered proppants) are treated with the fluorinated siloxane prior to injection into the fracture. In some embodiments, the
25 particles are treated with at least one fluorinated siloxane precursor during injection into the fracture, wherein the fluorinated siloxane precursor is converted to the fluorinated siloxane. In some embodiments of the present invention, the fluorinated siloxane is bonded to the particles. In some embodiments, the particles are at least 100 micrometers (in some embodiments, at least 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200,
30 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2500, or even at least 3000 micrometers; in some embodiments, in a range from 500 micrometers to 1700 micrometers) in size. In some embodiments, the treated particles have particle sizes in a range from 100

micrometers to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some
embodiments, in a range from 1000 micrometers to 3000 micrometers, 1000 micrometers
to 2000 micrometers, 1000 micrometers to 17000 micrometers (i.e., about 18 mesh to
about 12 mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12
5 mesh), 850 micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600
micrometers to 1200 micrometers (i.e., 30 mesh to about 16 mesh), 425 micrometers to
850 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers
(i.e., about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60
mesh to about 40 mesh), 200 micrometers to 425 micrometers (i.e., about 70 mesh to
10 about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70
mesh). In some embodiments, the treated particles are included with a plurality of other
particles (i.e., a plurality of particles comprising the treated particles). In some
embodiments, these particles collectively have particles in a range from 100 micrometers
to 3000 micrometers (i.e., about 140 mesh to about 5 mesh) (in some embodiments, in a
15 range from 1000 micrometers to 3000 micrometers, 1000 micrometers to 2000
micrometers, 1000 micrometers to 1700 micrometers (i.e., about 18 mesh to about 12
mesh), 850 micrometers to 1700 micrometers (i.e., about 20 mesh to about 12 mesh), 850
micrometers to 1200 micrometers (i.e., about 20 mesh to about 16 mesh), 600 micrometers
to 1200 micrometers (i.e., about 30 mesh to about 16 mesh), 425 micrometers to 850
20 micrometers (i.e., about 40 to about 20 mesh), 300 micrometers to 600 micrometers (i.e.,
about 50 mesh to about 30 mesh), 250 micrometers to 425 micrometers (i.e., about 60
mesh to about 40 mesh), 200 micrometers to 425 micrometers (i.e., about 70 mesh to
about 40 mesh), or 100 micrometers to 200 micrometers (i.e., about 140 mesh to about 70
mesh). In some embodiments, the “collective” plurality of particles comprises at least 5,
25 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even
at least 100 percent by weight of the treated particles.

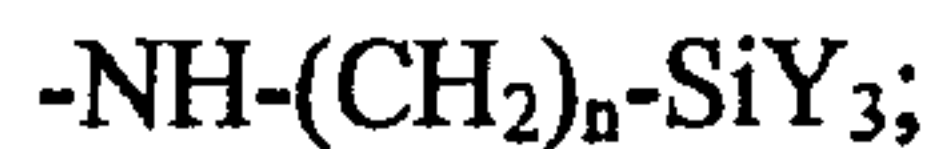
[009] In some embodiments, the fluorinated siloxane comprises a condensation product
of at least one fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula

30 $-O-(CH_2)_nN(R^4)S(O)_2-Rf^3$, and

at least one end group represented by the formula

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wherein

R^4 is alkyl having one to four carbon atoms

Rf^3 is a perfluoroalkyl group having from one to eight carbon atoms;

5 each Y is independently selected from the group consisting of hydroxyl, alkoxy, acyloxy, and halogen; and

each n is independently an integer from 1 to 4.

[0009a] In the embodiments above, the Q may have at least 2 and not more than 25 carbon atoms.

[0010] Treated proppants described herein are useful, for example, in facilitating the removal of fracturing fluids that have been injected into subterranean formation, including increasing the removal rate of the fracturing fluid. While not wanting to be bound by theory, it is believed this enhanced back-production of the fracturing fluids is due to the fluorinated siloxane altering the wettability of the proppant, thus rendering the proppant hydrophobic, oleophobic, and non-wetted by the fracturing fluids. An additional advantage of enhancing the fluid production from the fracture comprising the proppant treated with the fluorinated siloxane is thought to be the reduction in turbulent flow that should significantly reduce non-Darcy effects. Non-Darcy effects can effectively reduce the conductivity of a fracture by reducing fluid production.

[0011] Advantages embodiments of treated particle having a plurality of pores is that the treated particle has at least one of water or oil imbibition up to 95% as compared to a comparable, untreated particle.

Detailed Description

[0012] Exemplary particles for practicing the present invention include those known in the art for use as proppants in fractured subterranean geological formations comprising hydrocarbons, and include engineered proppants (e.g., resin coated sand, sintered bauxite, crystalline ceramic bubbles, ceramic (e.g., glass) beads, and sand graded to desired industry standards). The term "ceramic" as used herein refers to glasses, crystalline ceramics, glass-ceramics, and combinations thereof. Suitable particles can be made by techniques known in the art and/or obtained from commercial sources. Exemplary particles include those made of a material selected from the group consisting of sand,

thermoplastic, clay, glass, and alumina (e.g., sintered bauxite). Examples of particles include sand, clay-based particles, thermoplastic particles, and sintered bauxite particles. Sand proppants are available, for example, from Badger Mining Corp., Berlin, WI; Borden Chemical, Columbus, OH; Fairmont Minerals, Chardon, OH. Thermoplastic proppants are available, for example, from the Dow Chemical Company, Midland, MI; and BJ Services, Houston, TX. Clay-based proppants are available, for example, from CarboCeramics, Irving, TX; and Saint-Gobain, Courbevoie, France. Sintered bauxite ceramic proppants are available, for example, from Borovichi Refractories, Borovichi, Russia; 3M Company, St. Paul, MN; CarboCeramics, and Saint Gobain. Engineered proppants such as glass bead and ceramic microsphere proppants are available, for example, from Diversified Industries, Sidney, British Columbia, Canada; and 3M Company.

[0013] In some embodiments, fluorinated siloxanes useful in practicing the present invention comprise a condensation product of a reactive fluorinated silane represented by the formula (I):



wherein Rf, Q, Y, R¹, x, y, and z are as defined above. Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-. Rf can be a linear, branched, and/or cyclic structure, that may be saturated or unsaturated. The term "perfluoroalkyl group" includes groups in which all C-H bonds are replaced by C-F bonds as well as groups in which hydrogen or chlorine atoms are present instead of fluorine atoms provided that not more than one atom of either hydrogen or chlorine is present for every two carbon atoms. In some embodiments, when hydrogen and/or chlorine are present, Rf includes at least one perfluoromethyl group.

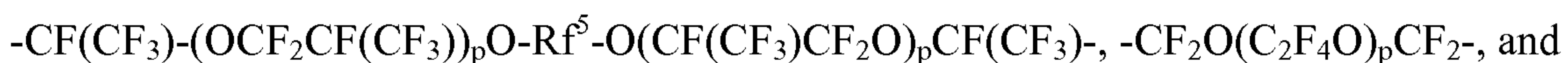
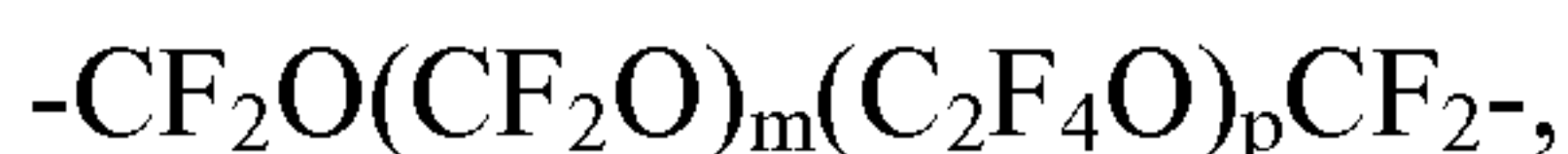
[0014] In some embodiments, Rf is a monovalent perfluoroalkyl group of formula (C_nF_{2n+1}), wherein n is an integer from 1 to 20 (in some embodiments, from 3 to 12 or even from 3 to 8). In some embodiments, Rf is C₄F₉.

[0015] In some embodiments, Rf is a perfluoropolyether group having two or more in-chain oxygen atoms. In some embodiments, the perfluoropolyether group comprises perfluorinated repeating units selected from the group consisting of -(C_nF_{2n})-, -(C_nF_{2n}O)-, -(CF(Rf⁴))-, -(CF(Rf⁴)O)-, -(CF(Rf⁴)C_nF_{2n}O)-, -(C_nF_{2n}CF(Rf⁴)O)-, -(CF₂CF(Rf⁴)O)-, and

combinations thereof (in some embodiments, $-(C_nF_{2n}O)-$, $-(CF(Rf^4)O)-$, $-(CF(Rf^4)C_nF_{2n}O)-$, $-(C_nF_{2n}CF(Rf^4)O)-$, $-(CF_2CF(Rf^4)O)-$, and combinations thereof); wherein Rf^4 is a perfluoroalkyl group, a perfluoroalkoxy group, or a perfluoroether group, each of which can be linear, branched, or cyclic, and can have 1 to 9 carbon atoms and up to 4 oxygen atoms; and n is an integer from 1 to 12 (in some embodiments, from 1 to 6, from 1 to 4, or even from 1 to 3). The perfluorinated repeating units may be arranged randomly, in blocks, or in alternating sequence.

[0016] In some embodiments, Rf is a monovalent (i.e., z is 1) perfluoropolyether group. In some of these embodiments, Rf is terminated with $C_nF_{2n+1}-$, $C_nF_{2n+1}O-$, or $X'C_nF_{2n}O-$, wherein X' is a hydrogen or chlorine atom. In some of these embodiments, the terminal group is $C_nF_{2n+1}-$ or $C_nF_{2n+1}O-$, wherein n is an integer from 1 to 6 or from 1 to 3. In some of these embodiments, the approximate average structure of Rf is $C_3F_7O(CF(CF_3)CF_2O)_pCF(CF_3)-$ or $CF_3O(C_2F_4O)_pCF_2-$, wherein the average value of p is 3 to 50.

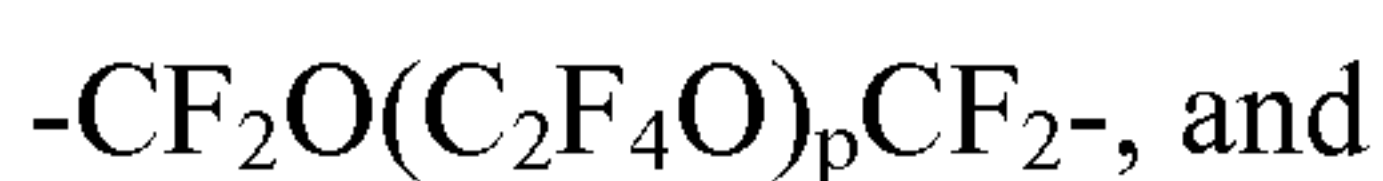
[0017] In some embodiments, Rf is a divalent (i.e., z is 2) perfluoropolyether group. In some of these embodiments, Rf is selected from the group consisting of



least one carbon atom and optionally interrupted in chain by O or N; m is 1 to 50; and p is

3 to 40. In some embodiments, Rf^5 is (C_nF_{2n}) , wherein n is 2 to 4. In some embodiments,

Rf is selected from the group consisting of $-CF_2O(CF_2O)_m(C_2F_4O)_pCF_2-$,



the average value of $m+p$ or p or $p+p$, respectively, is from about 4 to about 24. In some embodiments, p and m may be non-integral.

[0018] The divalent or trivalent organic linking group, Q , can be a linear, branched, or cyclic structure, that may be saturated or unsaturated and optionally contains one or more heteroatoms selected from the group consisting of sulfur, oxygen, and nitrogen, and/or optionally contains one or more functional groups selected from the group consisting of ester, amide, sulfonamide, carbonyl, carbonate, urea, and carbamate. Q includes at least 2

carbon atoms and not more than about 25 carbon atoms (in some embodiments, not more than 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, or even not more than 10 carbon atoms). When two, three, or four Q groups are present, each Q is independently selected. In some embodiments, Q is a linear hydrocarbon containing 1 to about 10 carbon atoms, optionally containing 1 to 4 heteroatoms and/or 1 to 4 functional groups. In some of these

[0019] Exemplary divalent Q groups include $-\text{SO}_2\text{NR}^2(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$,

$-\text{CON}(\text{R}^2)(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$, $-(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$, $-\text{C}(\text{O})\text{N}(\text{R}^2)-(\text{CH}_2)_k-$,

$-\text{CH}_2\text{CH}(\text{O-alkyl})\text{CH}_2\text{O}(\text{O})\text{C}-$, $-(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$, $-(\text{CH}_2)_k\text{SC}(\text{O})-$,

$-(\text{CH}_2)_k\text{O}(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$, $-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$, $-(\text{CH}_2)_k\text{SO}_2(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$,

$-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{OC}(\text{O})-$, $-(\text{CH}_2)_k\text{SO}_2\text{N}(\text{R}^2)(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$, $-(\text{CH}_2)_k\text{SO}_2-$,

$-\text{SO}_2\text{N}(\text{R}^2)(\text{CH}_2)_k\text{O}(\text{CH}_2)_k-$, $-\text{SO}_2\text{N}(\text{R}^2)(\text{CH}_2)_k-$, $-(\text{CH}_2)_k\text{O}(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$,

$-(\text{CH}_2)_k\text{SO}_2\text{N}(\text{R}^2)(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$, $-(\text{CH}_2)_k\text{SO}_2(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$,

$-\text{CON}(\text{R}^2)(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$, $-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$,

$-\text{CH}_2\text{CH}(\text{O-alkyl})\text{CH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$, $-\text{SO}_2\text{N}(\text{R}^2)(\text{CH}_2)_k\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$,

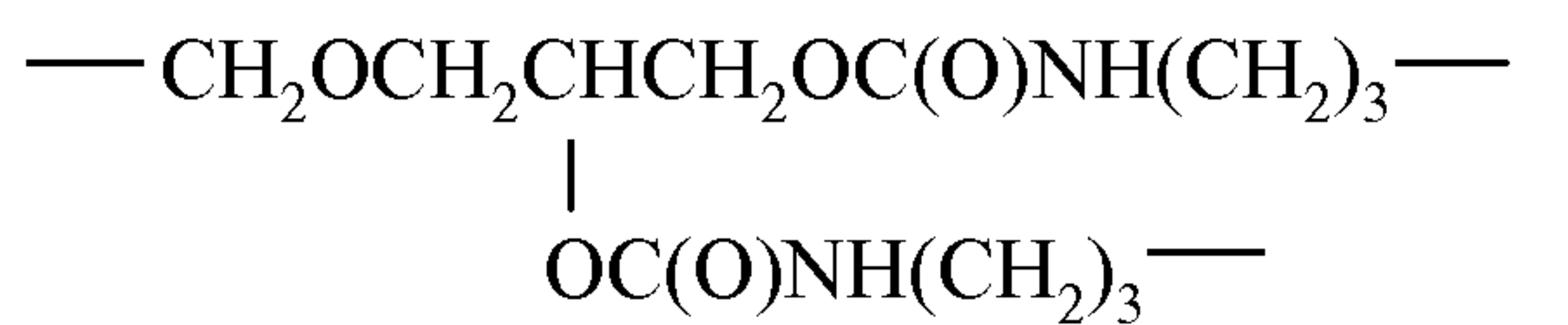
$-(\text{CH}_2)_k\text{O}(\text{CH}_2)_k-$, $-\text{CH}_2\text{O}-(\text{CH}_2)_k-$, $-\text{OC}(\text{O})\text{N}(\text{R}^2)(\text{CH}_2)_k-$, $-(\text{CH}_2)_k\text{N}(\text{R}^2)-$,

$-\text{C}_k\text{H}_{2k}-\text{OC}(\text{O})\text{NH}-$, $-(\text{CH}_2)_k\text{N}(\text{R}^2)\text{C}(\text{O})\text{O}(\text{CH}_2)_k-$,

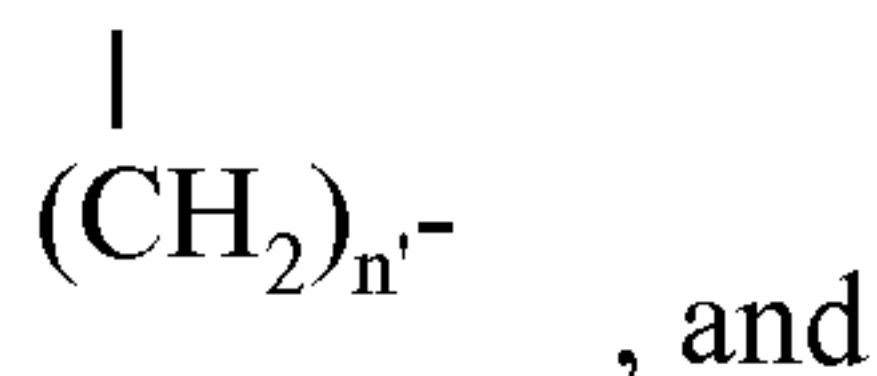
$-(\text{CH}_2)_k-$, $-\text{C}_k\text{H}_{2k}-$, $-\text{C}(\text{O})\text{S}-(\text{CH}_2)_k-$, and $-\text{CH}_2\text{OC}(\text{O})\text{N}(\text{R}^2)-(\text{CH}_2)_k-$, wherein R^2 is

hydrogen, C_{1-4} alkyl, or phenyl; and k is 2 to about 25 (in some embodiments, 2 to 15 or even 2 to 10).

[0020] Exemplary trivalent Q groups include



$-\text{S}(\text{O})_2-\text{N}(\text{R}^2)-(\text{C}_m\text{H}_{2m})-\text{N}-\text{S}(\text{O})_2-$



$-\text{S}(\text{O})_2-\text{N}(\text{R}^2)-(\text{C}_n\text{H}_{2n})-\text{CH}-(\text{C}_m\text{H}_{2m})-\text{N}(\text{R}^2)-\text{S}(\text{O})_2-$



, wherein R^2 is hydrogen,

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C₁₋₄ alkyl, or phenyl; each n and m are independently integers from 1 to 20 (in some embodiments, from 1 to 6 or even from 1 to 4); m' is an integer from 1 to 20 (in some embodiments, from 1 to 10 or even from 1 to 3); Q² is selected from the group consisting of -C(O)NH-(CH₂)_n- and -(CH₂)_n-, wherein n' is an integer from 0 to 4; and
 5 X is selected from the group consisting of -NH-, -O-, and -S-.

[0021] Each Y in Formula I is selected from the group consisting of hydroxyl, alkoxy (e.g., of 1 to 4 or even 1 to 2 carbon atoms), aryloxy (e.g., phenoxy), acyloxy (e.g., of 1 to 4 or even 1 to 2 carbon atoms), polyalkyleneoxy, and halogen (e.g., Cl or Br). "Polyalkyleneoxy" refers to -O-(CHR⁵-CH₂O)_q-R³ wherein R³ is C₁₋₄ alkyl, R⁵ is hydrogen
 10 or methyl, with at least 70% of R⁵ being hydrogen, and q is 1 to 40, or even 2 to 10. In some embodiments, each Y is independently a hydrolyzable group selected from the group consisting of alkoxy (e.g., of 1 to 4 or even 1 to 2 carbon atoms), aryloxy (e.g., phenoxy), and halogen (e.g., Cl or Br). These hydrolysable groups are capable of hydrolyzing, for example, in the presence of water, optionally under acidic or basic conditions, producing
 15 groups capable of undergoing a condensation reaction, for example silanol groups. In some embodiments, R is alkyl of one to six carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl). In some embodiments, R is aryl (e.g., phenyl). In some embodiments, x is 0. In some embodiments, x is 1.

[0022] Some reactive fluorinated silanes of formula I are commercially available, for example, as a fluorinated disilane (available, for example, from 3M Company under the trade designation "3M EASY CLEAN COATING ECC-1000"); a fluorinated silane (available, for example, from Daikin Industries, Inc., New York, NY under the trade designation "OPTOOLTM DSX"); tridecafluorooctyl functional silanes (available, for example, from United Chemical Technologies, Inc., Bristol, PA under the trade
 20 designation "PETRARCHTM" (e.g., grades "T2492" and "T2494"); and a 10% by weight fluorinated disilane solution (available, for example, from 3M Company under the trade designation "3M EASY CLEAN COATING ECC-4000").

[0023] The compounds of formula I described above can be synthesized using conventional synthetic methods. For example, when R_f is a perfluoropolyether group, perfluoropolyether esters or functional derivatives thereof can be combined with a
 30 functionalized alkoxy silane, such as a 3-aminopropylalkoxysilane, according to the

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method described in U. S. Pat. No. 3,810,874 (Mitsch et al.).

It will be understood that functional groups other than esters may be used with equal facility to incorporate silane groups into a perfluoropolyether. Some perfluoropolyether diesters are commercially available (e.g.,
 5 $\text{CH}_3\text{OC}(\text{O})\text{CF}_2(\text{OCF}_2\text{CF}_2)_{9-10}(\text{OCF}_2)_{9-10}\text{CF}_2\text{C}(\text{O})\text{OCH}_3$, a perfluoropolyether diester available, for example, from Solvay Solexis, Houston, TX, under the trade designation "FOMBLIN ZDEAL"). Other perfluoropolyether diesters may be prepared, for example, through direct fluorination of a hydrocarbon polyether diester by methods known in the art (see, e.g., U.S. Pat. Nos. 5,578,278 (Fall et al.) and 5,658,962 (Moore et al.)).

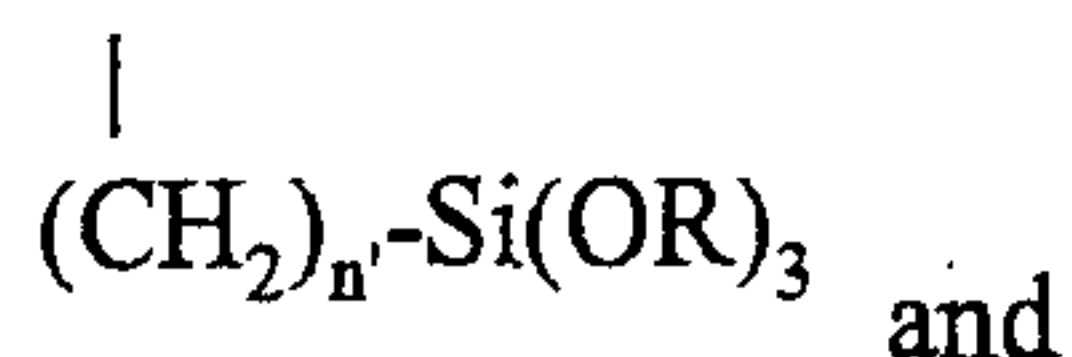
10 Perfluoropolyether diesters

(and perfluoropolyether monoesters) can also be prepared, for example, by oligomerization of hexafluoropropylene oxide (HFPO) and functionalization of the resulting perfluoropolyether carbonyl fluoride according to the methods described in U.S. Pat. No. 4,647,413 (Savu). An

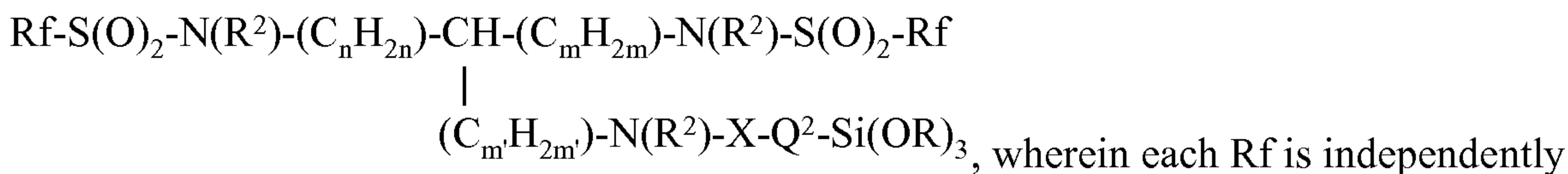
15 exemplary fluorinated silane of formula I wherein Rf is a divalent perfluoropolyether group is $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCOCF}_2(\text{OCF}_2\text{CF}_2)_{9-10}(\text{OCF}_2)_{9-10}\text{CF}_2\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$.

[0024] The above-described polyfluoropolyether silanes typically include a distribution of oligomers and/or polymers, and above structures are approximate average structures where the approximate average is over this distribution. These distributions may also contain
 20 perfluoropolyethers with no silane groups or more than two silane groups. Typically, distributions containing less than about 10% by weight of compounds without silane groups can be used.

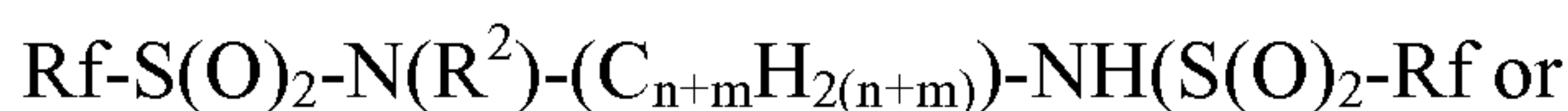
[0025] Methods of making fluorinated silanes of the formula I, wherein Rf is a monovalent perfluoroalkyl group, are known in the art (e.g., by alkylation of fluorinated
 25 alcohols or sulfonamides with chloroalkyltrialkoxysilanes, or alkylation with allyl chloride followed by hydrosilation with HSiCl_3) (see, e.g., U.S. Pat. No. 5,274,159 (Pellerite et al.)), Fluorinated silanes



represented by the formulas



$\text{C}_p\text{F}_{2p+1}$, wherein p is 1 to 8 and R^2 , R , m , n , m' , n' , X , and Q^2 are as defined above, can be prepared, for example, by similar methods (e.g., by alkylation of



5 $\text{Rf-S(O)}_2\text{-N(R}^2\text{)-(C}_n\text{H}_{2n}\text{)-CH(OH)-(C}_m\text{H}_{2m}\text{)-N(R}^2\text{)-S(O)}_2\text{-Rf}$), respectively, with chloroalkyltrialkoxysilanes) or by reaction of

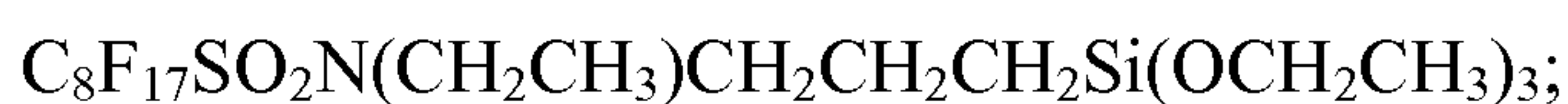


isocyanatoalkyltrialkoxysilanes as described in U.S. Pat. App. Pub. No. 2006/0147645 (Dams et al.), the disclosure of which is incorporated herein by reference.

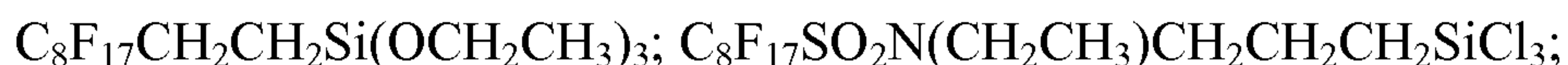
10 [0026] Perfluoroalkyl silanes of formula I, wherein Rf is a monovalent perfluoroalkyl group, include, for example, any one or any combination of the following:



15 $\text{C}_7\text{F}_{15}\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCl(OCH}_3\text{)}_2; \text{C}_7\text{F}_{15}\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_2(\text{OC}_2\text{H}_5);$



20 $\text{C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3\text{)}_3; \text{C}_4\text{F}_9\text{SO}_2\text{N(CH}_3\text{)CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3\text{)}_3;$

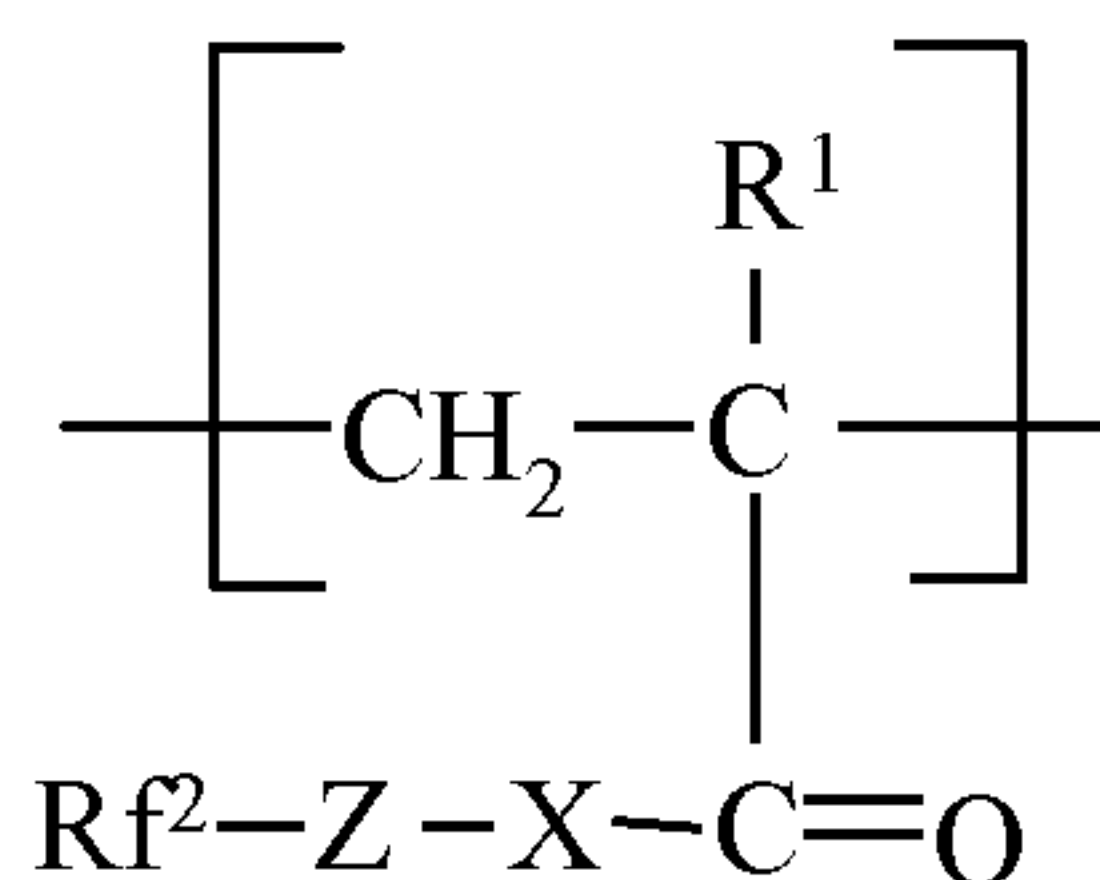


25 $[\text{C}_4\text{F}_9\text{S(O)}_2\text{N(CH}_3\text{)CH}_2\text{]}_2\text{CHOC(O)NHCH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3\text{)}_3$, and

$\text{C}_4\text{F}_9\text{S(O)}_2\text{N(CH}_3\text{)CH}_2\text{CH}_2\text{CH}_2\text{N(S(O)}_2\text{C}_4\text{F}_9\text{)CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3\text{)}_3$. Suitable fluorinated silanes of formula I include a mixture of isomers (e.g., a mixture of compounds containing linear and branched perfluoroalkyl groups).

[0027] In some embodiments, fluorinated siloxanes useful in practicing the present invention comprise a condensation product of a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula (II):

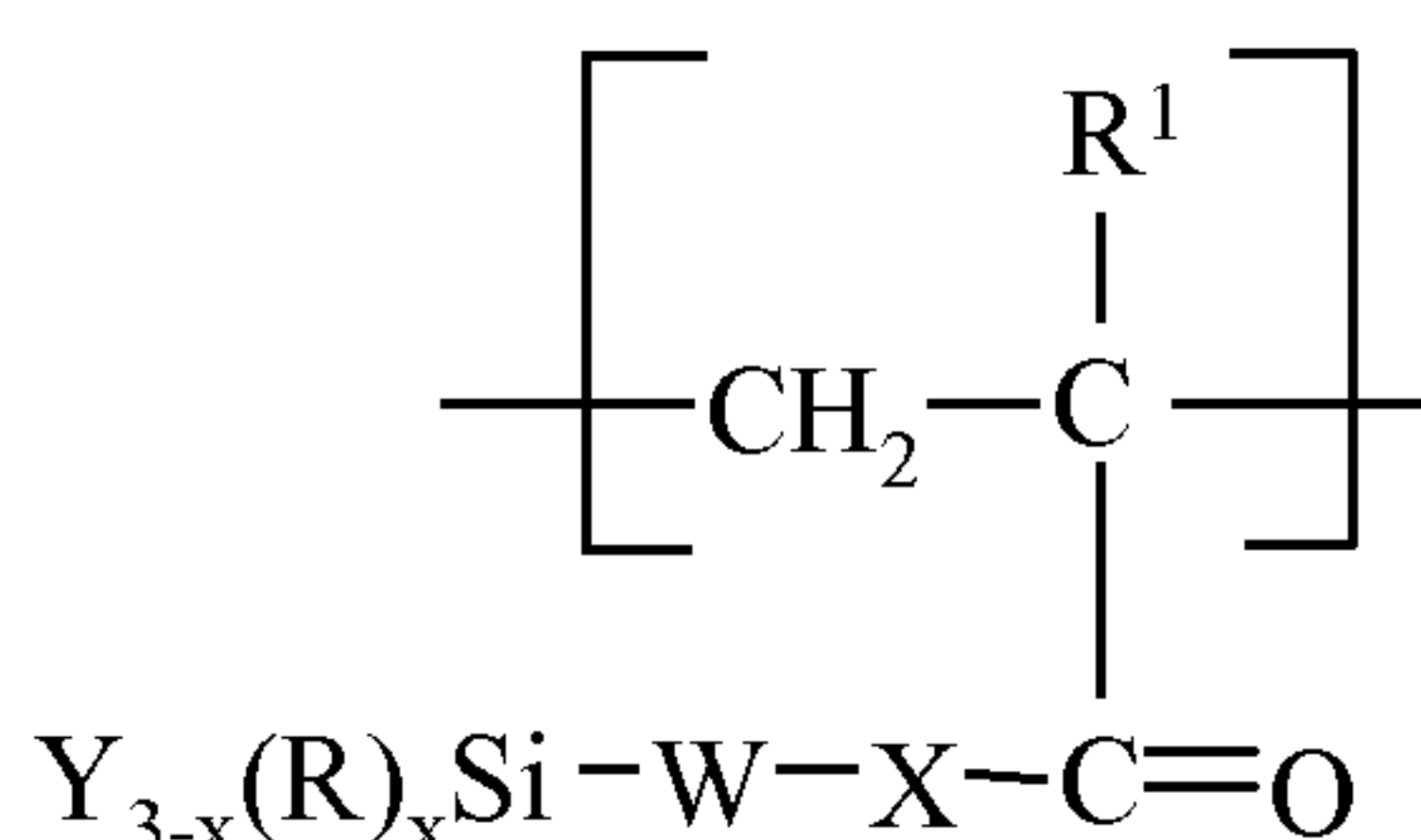


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II, and

at least one of

at least one divalent unit represented by the formula (III):



III, or

a chain-terminating group represented by the formula (IV):

10



wherein, Rf², R¹, R, W, X, Y, Z, and x are as defined above.

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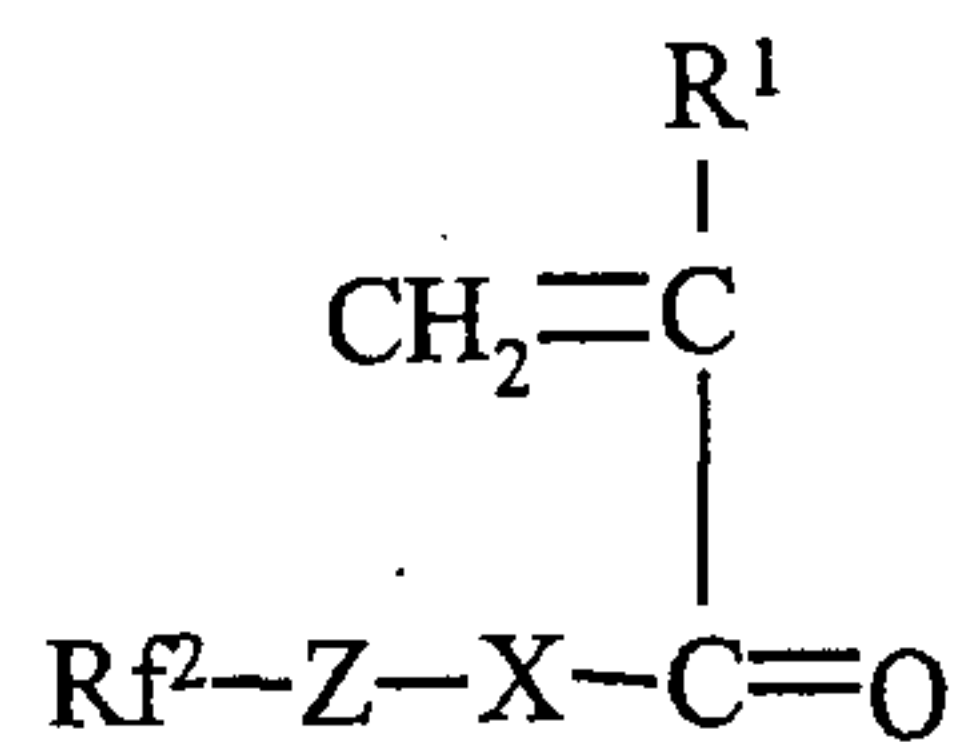
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[0028] The term "polymeric" refers to both oligomers and polymers. In some embodiments, the number of units represented by formula II is in a range from 1 to 100 (in some embodiments from 1 to 20). In some embodiments, the units represented by formula II are present in a range from 40% by weight to 80% by weight (or even from 50% to 75% by weight) based on the total weight of the polymeric fluorinated composition. In some embodiments, the number of units represented by formula III is in a range from 0 to 100 (or even from 0 to 20). In some embodiments, the units represented by formula III are present in a range from 1% to 20% by weight (or even 2% to 15% by weight) based on the total weight of the polymeric fluorinated composition. In some embodiments, the polymeric fluorinated composition contains at least 5 mole % (based on total moles of monomers) of Y groups. In some embodiments, the polymeric fluorinated composition has a number average molecular weight in a range from 400 to 100000, from 3500 to 100000, or even from 10000 to 75000 grams per mole or in a range from 600 to 20000, or even from 1000 to 10000 grams per mole. It will be appreciated by one skilled in the art

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that the polymeric fluorinated compositions useful in the present invention exist as a mixture of compounds.

[0029] A divalent unit of formula II is introduced into a polymeric fluorinated composition by polymerizing a monomer of the formula (IIa):



IIa.

Fluorochemical monomers of formula IIa and methods for the preparation thereof are known in the art (see, e.g., U.S. Pat. No. 2,803,615 (Ahlbrecht et al.)). Examples of such compounds include, for example, acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, perfluoroalkyl acrylates or methacrylates as disclosed in U.S. Pat. No. 5,852,148 (Behr et al.), perfluoropolyether acrylates or methacrylates as described in U.S. Pat. No. 4,085,137 (Mitsch et al.), and fluorinated acrylamides, methacrylamides, thioacrylates, and meththioacrylates as described in U.S. Pat. No. 6,689,854 (Fan et al.).

[0030] In some embodiments of formulas II and IIa, Rf^2 is a monovalent perfluoroalkyl group described above for Rf in embodiments of a compound of formula I.

[0031] The divalent organic linking group, Z, can be a linear, branched, or cyclic structure, that may be saturated or unsaturated and optionally contains one or more heteroatoms selected from the group consisting of sulfur, oxygen, and nitrogen, and/or optionally contains one or more functional groups selected from the group consisting of ester, amide, sulfonamide, carbonyl, carbonate, ureylene, and carbamate. Z includes at least 1 carbon atom and not more than about 25 carbon atoms (in some embodiments, not more than 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, or even not more than 10 carbon atoms). In some embodiments of formulas II and IIa, Z is a divalent organic linking group as described above for divalent Q groups. In some embodiments of formulas II and IIa, Z is $-\text{C}_y\text{H}_{2y}-$, $-\text{CON}(\text{R}^1)\text{C}_y\text{H}_{2y}-$, $-\text{SO}_2\text{N}(\text{R}^1)\text{C}_y\text{H}_{2y}-$, or -

$C_yH_{2y}SO_2N(R^1)C_yH_{2y}-$, wherein R^1 is hydrogen, or alkyl of one to four carbon atoms, and y is independently an integer from 1 to 6 (in some embodiments from 2 to 4). In some embodiments, R^1 is hydrogen. In some embodiments, R^1 is alkyl of one to four carbon atoms.

5 [0032] Examples of fluorinated monomers of formula IIa include:

$C_4F_9SO_2N(CH_3)C_2H_4OC(O)CH=CH_2$; $C_5F_{11}SO_2N(C_2H_5)C_2H_4OC(O)CH=CH_2$;

$C_6F_{13}SO_2N(C_2H_5)C_2H_4OC(O)C(CH_3)=CH_2$;

$C_3F_7SO_2N(C_4H_9)C_2H_4OC(O)CH=CH_2$;

$C_4F_9CH_2CH_2OC(O)CH=CH_2$; $C_5F_{11}CH_2OC(O)CH=CH_2$;

10 $C_6F_{13}CH_2CH_2OC(O)CH=CH_2$; $CF_3(CF_2)_2CH_2OC(O)CH=CH_2$,

$CF_3(CF_2)_2CH_2OC(O)C(CH_3)=CH_2$, $CF_3(CF_2)_3CH_2OC(O)C(CH_3)=CH_2$,

$CF_3(CF_2)_3CH_2OC(O)CH=CH_2$,

$CF_3(CF_2)_3S(O)_2N(R^a)-(CH_2)_2-OC(O)CH=CH_2$,

$CF_3(CF_2)_3S(O)_2N(R^a)-(CH_2)_2-OC(O)C(CH_3)=CH_2$,

15 $CF_3CF_2(CF_2CF_2)_{2-8}(CH_2)_2OC(O)CH=CH_2$,

$CF_3(CF_2)_7S(O)_2N(R^a)-(CH_2)_2-OC(O)CH=CH_2$,

$CF_3(CF_2)_7S(O)_2N(R^a)-(CH_2)_2-OC(O)C(CH_3)=CH_2$,

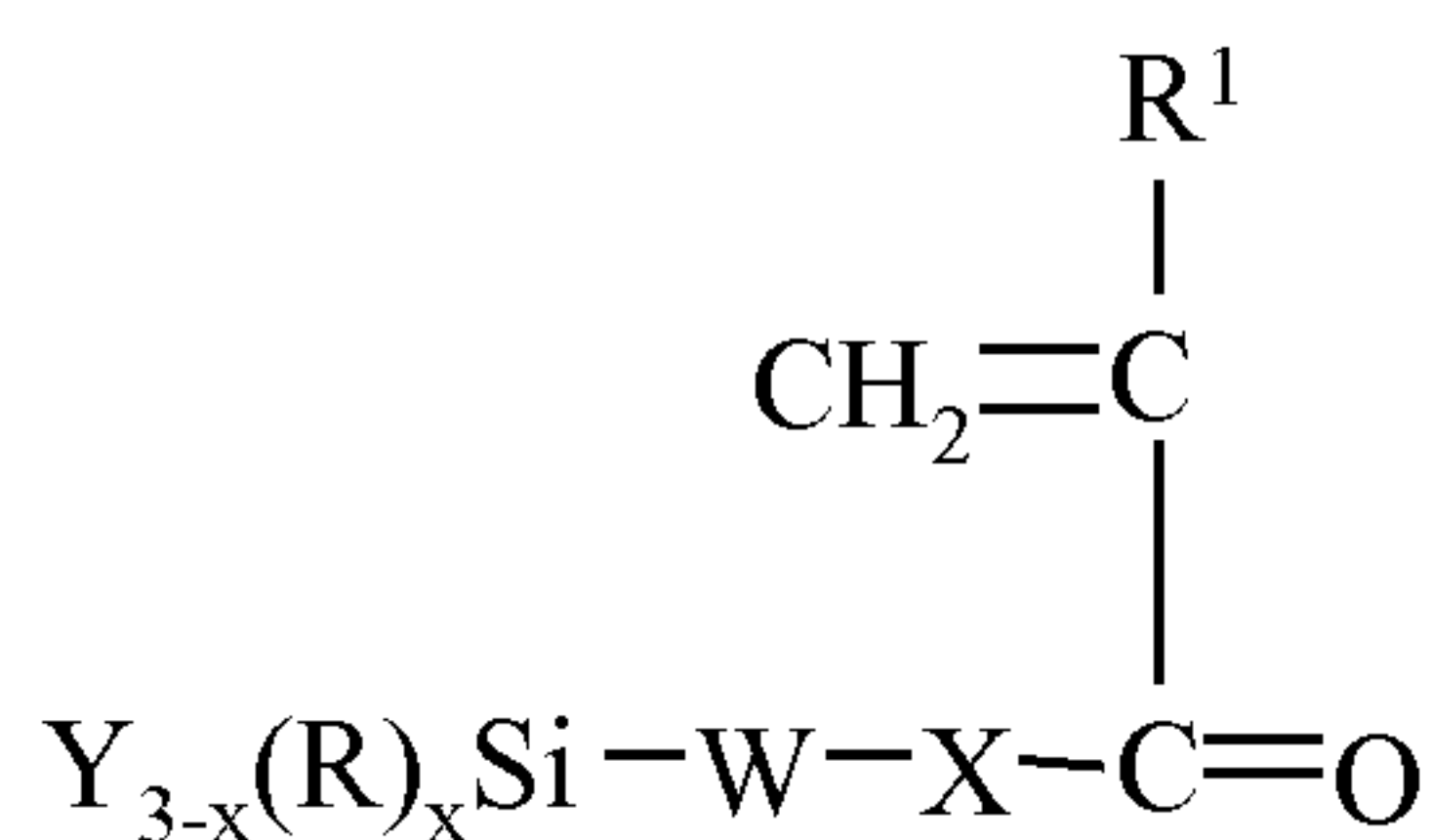
$CF_3(CF_2)_7CH_2CH_2S(O)_2N(CH_3)-(CH_2)_2-OC(O)C(CH_3)=CH_2$,

$CF_3O(CF_2CF_2)_uCH_2OC(O)CH=CH_2$, $CF_3O(CF_2CF_2)_uCH_2OC(O)C(CH_3)=CH_2$,

20 $C_3F_7O(CF(CF_3)CF_2O)_uCF(CF_3)CH_2OC(O)CH=CH_2$, and

$C_3F_7O(CF(CF_3)CF_2O)_uCF(CF_3)CH_2OC(O)C(CH_3)=CH_2$; wherein R^a represents methyl, ethyl or n-butyl, and u is about 1 to 50.

[0033] Polymeric fluorinated compositions according to the present invention may have a divalent unit represented by formula III. A divalent unit of formula III is introduced into a
25 polymeric fluorinated composition by copolymerizing a monomer of formula IIa with a monomer of the formula (IIIa):



IIIa,

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wherein R^1 , R, W, X, Y, and x are as defined above. In some embodiments of formula IIIa, the groups R^1 , R, Y, and x are those described above for embodiments of a compound of formula I. In some embodiments, W is alkylene of one to four carbon atoms. Some monomers of formula IIIa are commercially available (e.g.,

5 $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (available, for example, from Union Carbide, New York, NY, under the trade designation "A-174")); others can be made by conventional synthetic methods.

[0034] Polymeric fluorinated compositions according to the present invention may optionally include other interpolymerized divalent units, which may contain hydrophobic,

10 hydrophilic, or water-solubilizing groups. Useful monomers (including water-solubilizing monomers) that can be combined with those of formulas IIa and IIIa include non-fluorinated monomers described in U.S. Pat. Nos. 6,977,307 (Dams) and 6,689,854 (Fan et. al.).

[0035] Polymeric fluorinated compositions useful in practicing the present invention may

15 have a chain-terminating group represented by formula IV. A chain-terminating group of formula IV may be incorporated into a polymeric fluorinated composition, for example, by polymerizing monomers of formula IIa, optionally IIIa, and optionally at least one non-fluorinated monomer in the presence of a chain-transfer agent of the formula (IVa):



20 wherein R, W, Y, and x are as defined above. In some embodiments of formula IIIa, the groups R, Y, and x are those described above for embodiments of a compound of formula I. In some embodiments, W is alkylene of one to four carbon atoms. Some monomers of formula IVa are commercially available (e.g., 3-mercaptopropyltrimethoxysilane (available, for example, from Huls America, Inc.,

25 Somerset, N.J., under the trade designation "DYNASYLAN")); others can be made by conventional synthetic methods. A chain-terminating group of formula IV can also be incorporated into a polymeric fluorinated composition by polymerizing monomers of formula IIa, optionally IIIa, and optionally at least one non-fluorinated monomer in the presence of a hydroxyl-functional chain-transfer agent (e.g., 2-mercaptoethanol, 3-

30 mercapto-2-butanol, 3-mercapto-2-propanol, 3-mercapto-1-propanol, 3-mercapto-1,2-propanediol) and subsequent reaction of the hydroxyl functional group with, for example, a chloroalkyltrialkoxysilane. In a polymerization reaction to make a polymeric fluorinated

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composition, a single chain transfer agent or a mixture of different chain transfer agents may be used to control the number of polymerized monomer units in the polymer and to obtain the desired molecular weight of the polymeric fluorochemical silane.

5 [0036] The polymeric fluorinated oligomeric composition can conveniently be prepared through a free radical polymerization of a fluorinated monomer with optionally a non-fluorinated monomer (e.g., a water-solubilizing monomer) and at least one of a monomer containing a silyl group or a chain transfer agent containing a silyl group using methods known in the art. See, for example, the methods described in U.S. Pat. Nos. 6,977,307 (Dams) and 6,689,854 (Fan et. al.).

10

[0037] In some embodiments, fluorinated siloxanes useful in practicing the present invention comprise a condensation product of at least one fluorinated urethane oligomer of at least two repeat units (e.g., from 2 to 20 repeating units) comprising at least one end group represented by the formula $-O-Z-Rf^2$, and at least one end group represented by the formula $-X^1-W-SiY_{3-x}(R)_x$. In some embodiments, the fluorinated urethane oligomer of at least two repeat units comprises at least one end group represented by the formula $-O-(CH_2)_nN(R^4)S(O)_2-Rf^3$, and at least one end group represented by the formula $-NH-(CH_2)_n-SiY_3$, wherein Z, Rf^2 , R^4 , Rf^3 , Y, and x are as defined above, and n is an integer from 1 to 4.

15

[0038] The term "urethane oligomer" refers to oligomers containing at least one of urethane or urea functional groups. In some embodiments, the at least one fluorinated urethane oligomer of at least two repeat units comprises the reaction product of (a) at least one polyfunctional isocyanate compound; (b) at least one polyol; (c) at least one fluorochemical monoalcohol; (d) at least one silane; and optionally (e) at least one water-solubilizing compound comprising at least one water-solubilizing group and at least one isocyanate-reactive hydrogen containing group. In some embodiments, at least one polyamine may also be used.

20

[0039] Fluorine urethane oligomers useful in the present invention may be prepared, for example, by reaction of at least one polyfunctional isocyanate with at least one polyol and reaction of the resulting oligomer with at least one fluorinated monoalcohol and at least one silane. Exemplary reaction conditions, polyfunctional isocyanates, polyols,

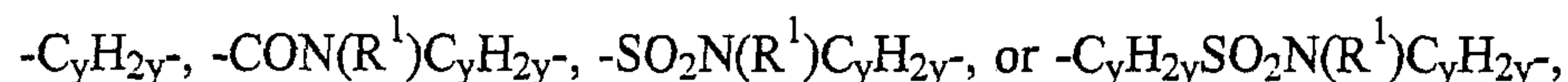
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fluorochemical monoalcohols, silanes, and water-solubilizing compounds are described in U.S. Pat. No. 6,646,088 (Fan et al.).

[0040] In some embodiments of formula $-O-Z-Rf^2$, Rf^2 is a monovalent perfluoroalkyl group described above for Rf in embodiments of a compound of formula I.

[0041] The divalent organic linking group, Z, in formula $-O-Z-Rf^2$, can be a linear, branched, or cyclic structure, that may be saturated or unsaturated and optionally contains one or more heteroatoms selected from the group consisting of sulfur, oxygen, and nitrogen, and/or optionally contains one or more functional groups selected from the group consisting of ester, amide, sulfonamide, carbonyl, carbonate, ureylene, and carbamate. Z includes at least 1 carbon atom and not more than about 25 carbon atoms (in some embodiments, not more than 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, or even not more than 10 carbon atoms). In some embodiments of formulas II and IIa, Z is a divalent organic linking group as described above for divalent Q groups. In some embodiments of formulas II and IIa, Z is



wherein R^1 is hydrogen or alkyl of one to four carbon atoms, and y is independently an integer from 1 to 6 (in some embodiments from 2 to 4). In some embodiments, Rf^3 is a perfluoroalkyl group having from 2 to 5 (e.g., 4) carbon atoms. An end-group of the formula $-O-Z-Rf^2$ ((in some embodiments,

$O-(CH_2)_nN(R^4)S(O)_2-Rf^3$) can be incorporated into a fluorinated urethane oligomer by carrying out the condensation polymerization reaction (e.g., as described above) in the presence of a fluorinated monoalcohol of formula $HO-Z-Rf^2$.

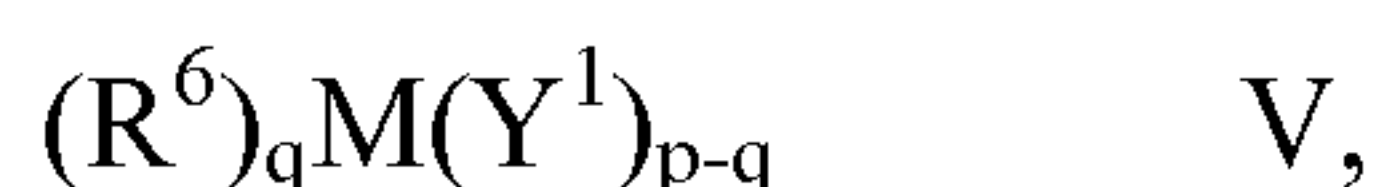
[0042] Useful fluorinated monoalcohols include, for example, 2-(N-methylperfluorobutanesulfonamido)ethanol; 2-(N-ethylperfluorobutanesulfonamido)ethanol; 2-(N-methylperfluorobutanesulfonamido)propanol; N-methyl-N-(4-hydroxybutyl)perfluorohexanesulfonamide; 1,1,2,2-tetrahydroperfluorooctanol; 1,1-dihydroperfluorooctanol; $C_6F_{13}CF(CF_3)CO_2C_2H_4CH(CH_3)OH$; n- $C_6F_{13}CF(CF_3)CON(H)CH_2CH_2OH$; $C_4F_9OC_2F_4OCF_2CH_2OCH_2CH_2OH$;

$C_3F_7CON(H)CH_2CH_2OH$; 1,1,2,2,3,3-hexahydroperfluorodecanol;
 $C_3F_7O(CF(CF_3)CF_2O)_{1-36}CF(CF_3)CH_2OH$; $CF_3O(CF_2CF_2O)_{1-36}CF_2CH_2OH$; and mixtures thereof. In some embodiments, the fluorinated monoalcohol is represented by the formula $HO-(C_nH_{2n})N(R^4)S(O)_2-Rf^3$.

- 5 [0043] An end-group of the formula $-X^1-W-SiY_{3-x}(R)_x$ can be incorporated into a fluorinated urethane oligomer by carrying out the polymerization reaction (e.g., as described above) in the presence of a silane of formula $HX^1-W-SiY_{3-x}(R)_x$ (in some embodiments, $H_2N-(CH_2)_n-SiY_3$). Useful aminosilanes include, for example, $H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$; $H_2NCH_2CH_2CH_2Si(OCH_3)_3$;
 10 $H_2NCH_2CH_2CH_2Si(O-N=C(CH_3)(C_2H_5))_3$; $HSCH_2CH_2CH_2Si(OCH_3)_3$;
 $HO(C_2H_4O)_3C_2H_4N(CH_3)(CH_2)_3Si(OC_4H_9)_3$; $H_2NCH_2C_6H_4CH_2CH_2Si(OCH_3)_3$;
 $HSCH_2CH_2CH_2Si(OCOCH_3)_3$; $HN(CH_3)CH_2CH_2Si(OCH_3)_3$;
 $HSCH_2CH_2CH_2SiCH_3(OCH_3)_2$; $(H_3CO)_3SiCH_2CH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$;
 $HN(CH_3)C_3H_6Si(OCH_3)_3$; $CH_3CH_2OOCCH_2CH(COOCH_2CH_3)HNC_3H_6Si(OCH_2CH_3)_3$;
 15 $C_6H_5NHC_3H_6Si(OCH_3)_3$; $H_2NC_3H_6SiCH_3(OCH_2CH_3)_2$;
 $HOCH(CH_3)CH_2OCONHC_3H_6Si(OCH_2CH_3)_3$;
 $(HOCH_2CH_2)_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$; and mixtures thereof.

[0044] Some fluorinated urethane oligomers useful in the present invention are commercially available (e.g., a 20% by weight aqueous fluoropolymer solution available
 20 from 3M Company under the trade designation "3M STAIN RESISTANT ADDITIVE SRC-220" and a 30% solution of fluorinated urethane silane available from 3M Company under the trade designation "PM-490").

[0045] In some embodiments, the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane, as described above, and a compound of the
 25 formula (V):



wherein M represents an element of valency $p+q$ selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn (in some embodiments selected from the group consisting of Ti, Zr, Si and Al); R^6 represents a non-hydrolysable group (e.g., an alkyl
 30 group of 1 to 20 carbon atoms which may be straight chained or branched and may include

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cyclic hydrocarbon structures, a C₆-C₃₀ aryl group, optionally substituted by one or more substituents selected from halogens and C₁-C₄ alkyl groups, or a C₇-C₃₀ arylalkyl group); p is 3 or 4 depending on the valence of M; q is 0,1 or 2; and Y¹ represents a hydrolysable group (e.g., alkoxy, acyloxy, and halogen). Compounds of formula V and formulations
5 containing compounds of formula V, fluorinated silanes, and optionally other crosslinking agents are described, for example, in U.S. Pat. No. 6,716,534 (Moore et al.).

[0046] Representative examples of compounds of formula V include tetramethoxysilane, tetraethoxysilane, methyl triethoxysilane, dimethyldiethoxysilane,
10 octadecyltriethoxysilane, methyl trichlorosilane, tetra-methyl orthotitanate, tetra ethyl orthotitanate, tetra-iso-propyl orthotitanate, tetra-n-propyl orthotitanate, tetraethyl zirconate, tetra-iso-propyl zirconate tetra-n-propyl zirconate. Mixtures of compounds of formula V may also be used in the preparation of fluorinated siloxanes.

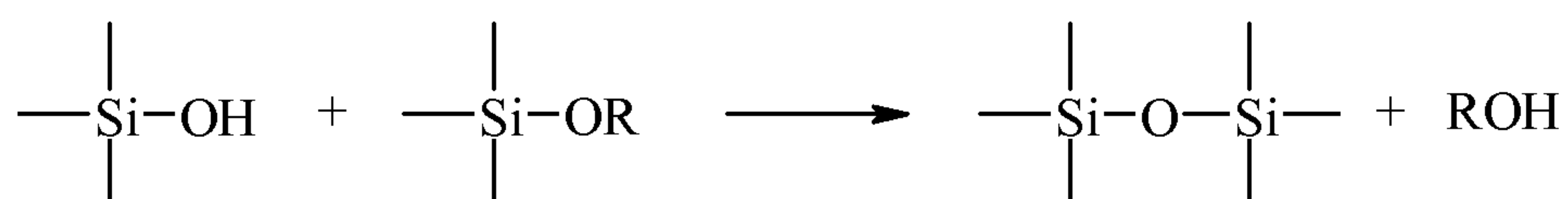
[0047] Typically the fluorinated silane is dissolved or dispersed in a dispersing medium
15 (e.g., water and/or organic solvent (e.g., alcohols, ketones, esters, alkanes and/or fluorinated solvents (e.g., hydrofluoroethers and/or perfluorinated carbons)) that is then applied to the particles. The amount of liquid medium used should be sufficient to allow the solution or dispersion to generally evenly wet the particles being treated. Typically, the concentration of the fluorinated silane in the solution/dispersion solvent is the range
20 from about 5% to about 20% by weight, although amounts outside of this range may also be useful. Some formulations containing fluorinated silanes (e.g., of formula I) that may be useful are included in U.S. Pat. No. 6,613,860 (Dams et al.).

The particles are typically treated with the fluorinated
silane solution/dispersion at temperatures in the range from about 25°C to about 50°C,
25 although temperatures outside of this range may also be useful. The treatment solution/dispersion can be applied to the particles using techniques known in the art for applying solutions/dispersions to particles (e.g., mixing the solution/dispersion and particles in a vessel (in some embodiments under reduced pressure) or spraying the solutions/dispersions onto the particles). After application of the treatment
30 solution/dispersion to the particles, the liquid medium can be removed using techniques known in the art (e.g., drying the particles in an oven). Typically, about 0.1 to about 5 (in

some embodiments, for example, about 0.5 to about 2) percent by weight fluorinated silane is added to the particles, although amounts outside of this range may also be useful.

[0048] Hydrolysis of the Y groups (i.e., alkoxy, acyloxy, or halogen) of reactive fluorinated silanes and other fluorinated siloxane precursors typically generates silanol groups, which participate in condensation reactions to form fluorinated siloxanes, for example, according to Scheme I, and/or participate in bonding interactions with silanol groups or other metal hydroxide groups on the surface of particles (including proppants). The bonding interaction may be through a covalent bond (e.g., through a condensation reaction) or through hydrogen bonding. Hydrolysis can occur, for example, in the presence of water optionally in the presence of an acid or base (in some embodiments, acid). The water necessary for hydrolysis may be added to a formulation containing the fluorinated silane that is used to coat the particles (e.g., proppants), may be adsorbed to the surface of the particles, or may be present in the atmosphere to which the fluorinated silane is exposed (e.g., an atmosphere having a relative humidity of at least 10%, 20%, 30%, 40%, or even at least 50%). Water (e.g., brine) may be present in a subterranean geological formation comprising hydrocarbons and may cause hydrolysis of hydrolysable groups on a fluorinated silane or other fluorinated siloxane precursor (and cause condensation to provide a fluorinated siloxane) during the injection of particles into a fracture of the formation.

20 Scheme I



[0049] Under neutral pH conditions, the condensation of silanol groups is typically carried out at elevated temperature (e.g., in a range from 40°C to 200°C or even 50°C to 100°C). Under acidic conditions, the condensation of silanol groups may be carried out at room temperature (e.g., in a range from about 15°C to about 30°C or even 20°C to 25°C). The rate of the condensation reaction is typically dependent upon temperature and the concentration of fluorinated silane (e.g., in a formulation containing the fluorinated silane).

[0050] Techniques for fracturing subterranean geological formation comprising hydrocarbons are known in the art, as are techniques for injecting proppants into the

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fractured formation to prop open fracture openings. In some methods, a hydraulic fluid is injected into the subterranean geological formation at rates and pressures sufficient to open a fracture therein. The fracturing fluid (usually water with specialty high viscosity fluid additives) when injected at the high pressures exceeds the rock strength and opens a fracture in the rock. Proppant particles described herein can be included in the fracturing fluid.

[0051] Optionally, conventional proppant materials can also be used together with the treated particles (including proppants) described herein.

[0052] Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

Example 1

[0053] A 5% by weight treatment solution was prepared by diluting a 20% by weight aqueous fluoropolymer solution (obtained from 3M Company, St. Paul, MN under the trade designation "3M STAIN RESISTANT ADDITIVE SRC-220") to 5% with isopropyl alcohol.

[0054] About 100 grams of an intermediate strength ceramic proppant (obtained under the trade designation "CARBOPROPTM 20/40"; (20/40 mesh) from Carboceramics, Irving, TX) were placed in a 500 milliliter (ml) flask. About 20 grams of the treatment solution was added to the proppant containing flask at 25°C. The contents of the flask was heated to about 50°C via a water bath and mixed for about 30 minutes. After mixing, the liquid medium (i.e., the solvent) was removed by using a rotary evaporator (obtained under the trade designation "ROTAVAPORTM" (Model R-124) from Brinkmann Instruments, Inc, Westbury, NY) under reduced pressure (about 50 mm Hg) at about 50°C. The treated proppant was then dried in the oven at about 70°C for about 3 hours. The weight percent of the active fluoropolymer added to the proppants was about 1% by weight.

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Example 2

[0055] Example 2 treated proppant was prepared as described for Example 1, except the treatment solution was prepared by diluting a 20% by weight aqueous fluoropolymer solution ("3M STAIN RESISTANT ADDITIVE SRC-220") to 5% with water. The weight percent of the active fluoropolymer added to the proppants was about 1% by weight.

Example 3

[0056] Example 3 treated proppant was prepared as described for Example 1, except the treatment solution was prepared by diluting a 10% by weight fluorinated disilane solution (obtained from 3M Company under the trade designation "3M EASY CLEAN COATING ECC-4000") to 5% by weight with ethanol. The weight percent of the active fluorinated disilane added to the proppants was about 1% by weight.

Example 4

[0057] Example 4 treated proppant was prepared as described for Example 1, except the treatment solution was prepared by diluting a 20% by weight aqueous fluoropolymer solution ("3M STAIN RESISTANT ADDITIVE SRC-220") to 10% with isopropyl alcohol. The weight percent of the active fluoropolymer added to the proppants was about 2% by weight.

Example 5

[0058] Example 5 treated proppant was prepared as described for Example 1, except the treatment solution was 5% by weight of 3-(N-Methylperfluorobutanesulfonamidopropyl)trimethoxysilane $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$ in ethanol. The synthesis of this material is described as follows: A mixture of about 626 grams (2 mol) of $C_4F_9SO_2N(CH_3)H$, generally made as described in U.S. Pat. No. 6,664,354 (Savu et al.), Example 1, Part A, about 432 grams (2 mol) of a 25% by weight

NaOMe in MeOH, and 100 ml of diglyme was stripped on a rotovapor to leave a soft solid.

[0059] The resulting solid was transferred to a 3 liter, 3-neck paddle-stirred flask with about 400 ml of diglyme. The contents of the flask was stirred at 50°C. About 400 grams
5 (2 mol) of $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ was added to the flask in a slow stream. The mixture was heated overnight at about 90°C. Gas Chromatography showed incomplete reaction. The contents of the flask was then heated to about 120°C for about 10 hours. Gas Chromatography showed the reaction was essentially complete. The resulting slurry was cooled to about 25°C, and the NaCl filtered out. The resulting cake was rinsed with
10 methylene chloride. The mixture was one-plate distilled to yield first diglyme at about 30°C/1 mmHg (133 Pa) and then product at about 100-120°C/0.3 mmHg (40 Pa). About 20 grams of the resulting 5% $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ was used to treat 100 grams of proppant ("CARBOPROP 20/40") as described in Example 1. The weight percent of $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ added to the proppants was about 1% by
15 weight.

Example 6

[0060] Example 6 treated proppant was prepared as described for Example 1, except the treatment solution was 10% by weight aqueous fluoropolymer solution. This treatment
20 solution was prepared by adding about 10 grams of water to about 10 grams of a 20% by weight aqueous fluoropolymer solution ("3M STAIN RESISTANT ADDITIVE SRC-220"). The weight percent of the active fluoropolymer added to the proppants was about 2% by weight.

Example 7

[0061] Example 7 treated proppant was prepared as described for Example 1, except the treatment solution was 5% by weight

$[\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2]_2\text{CHOC}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ in EtOH.

[0062] $[\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2]_2\text{CHOH}$ was prepared as follows. A three-necked round
30 bottom 1000-ml flask, fitted with a stirrer, heating mantle, condenser, nitrogen inlet, Dean-

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Stark trap and thermometer was charged with about 313 grams of $C_4F_9SO_2N(CH_3)H$ (1 mole (mol)), generally made as described in U.S. Pat. No. 6,664,354 (Savu et al.), Example 1, Part A, about 100 grams of *N,N*-dimethylformamide, and about 40 grams of heptane. The mixture was heated to reflux, and then dried by azeotropic distillation. The mixture was cooled to about 30°C under nitrogen purge, and about 180 grams of sodium methoxide (30% in methanol; 1 mol) was added. The mixture was heated at about 50°C for about 1 hour, stripping off methanol under vacuum from an aspirator. About 65 grams of 1,3-dichloro-2-propanol (0.5 mol) was added to the flask and the temperature was elevated to about 80°C and held overnight. The result mixture was washed with deionized water (about 300 ml at about 80°C) three times, and the remaining organic layer was separated and dried in an oven at about 120°C for about 1 hour. Vacuum distillation at about 150°C to about 200°C at about 0.1 to about 0.5 mm Hg (13 to 67 Pa) resulted in about 275 grams of product.

[0063] Next, $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$ was prepared as follows. A three-necked round bottom 500 ml flask fitted with a stirrer, heating mantle, condenser, nitrogen inlet, Dean-Stark trap and thermometer was charged with about 204.6 grams of the $[C_4F_9SO_2N(CH_3)CH_2]_2CHOH$ (0.3 mol), and about 250 grams methyl ethyl ketone. The mixture was heated for about 1 hour at about 100°C and about 50 grams of material was removed using the Dean-Stark trap. The mixture was cooled to about 30°C, and about 74.4 grams of $OCN(CH_2)_3Si(OCH_2CH_3)_3$ (0.3 mol), and three drops of stannous octanoate were added. The resulting mixture was heated at about 75°C under nitrogen for about 16 hours.

[0064] The weight percent of $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$ added to the proppants was about 2% by weight.

Example 8

[0065] Example 8 treated proppant was prepared as described for Example 1, except the treatment solution was 5% by weight of a copolymer of MeFBSEA/ODMA/A-174/HS(CH₂)₃Si(OCH₃)₃ at the molar ratio of (6:1:1:1) in isopropyl alcohol.

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[0066] 3-N-Methylperfluorobutanesulfonamidoethyl acrylate (N-MeFBSEA) was prepared according to the method of U.S. Pat. No. 6,664,354 (Savu), Example 2, Part B.

[0067] The of MeFBSEA/ODMA/A-174/HS(CH₂)₃Si(OCH₃)₃ was prepared as follows.

5 About 123.3 grams of the N-MeFBSEA, about 16.9 grams of octadecyl methacrylate (ODMA, obtained from Sigma-Aldrich, St Louis, MO), 11.8 grams of methylacryloxypropyltrimethoxysilane (obtained from Sigma-Aldrich), about 9.8 grams of (3-mercaptopropyl)trimethoxy silane (obtained from Sigma-Aldrich), about 1 gram of t-butylperoxoate, and about 163 grams of isopropyl alcohol were added to a 1 liter flask
10 equipped with an overhead stirrer, a thermocouple, and a reflux condenser with nitrogen flowing through the opening used for monomer addition. After the additions, the flask was kept under slight positive nitrogen pressure in order to exclude oxygen from the batch. The reactants were heated to about 80°C. Due to an initial exotherm, the batch heated itself to about 90°C. The heating was continued for 5 hours. The percent solid of the
15 polymer was about 50% by weight. The 50% by weight concentrate was diluted with isopropyl alcohol to 10% by weight solution for proppant treatment.

[0068] About 10 grams of the treatment solution was used to treat about 100 grams of proppant as described in Example 1. The weight percent of the active fluoropolymer added to the proppants was about 1% by weight.

20 [0069] The contact angles for treated proppant (after drying at about 70°C) were measured using a goniometer (obtained under the trade designation "KRUSSTM G120" from Kruss GmbH, Hamburg, Germany). Although not wanting to be bound by theory, it is believed, the measurement of the static, water and hexadecane contact angle provides a prediction of the surface properties of coated proppants. For each example, about 2 grams of coated
25 proppant was placed on a glass slide for measurement. The slide was gently tapped to form a thin layer of proppant on the slide. The average of 3 measurements for each of Examples 1-7 are provided in Table 1, below.

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Table 1

	Example	Static Water Contact Angle (degree)	Static Hexadecane Contact Angle (degree)
5	1	126	101
	2	123	86
	3	118	80
	4	117	87
	5	120	97
10	6	124	100
	7	110	84
	Untreated Proppant	absorbed	absorbed

[0070] The oil and water absorption (i.e., oil and water imbibition) of the examples was also measured. About 10 grams of treated proppant was immersed into about 20 grams of deionized water for about 1 hour. The water was filtered off with filter paper (Qualitative Grade 4); Whatman™ Filter Paper, Florham Park, NJ. The surface water was carefully removed with paper towel, and the proppant again weighed. The water absorption was then calculated based on the difference in weight before and after immersion in the water. The water absorptions values (an average of 2 measurements) for Examples 1-7 are provided in Table 2, below.

Table 2

	Example	Water Absorption (%)	Oil Absorption (%)	
25	1	0.75	1.6	
	2	0.9	2	
	3	1.3	2.6	
	4	0.55	0.8	
	30	5	5.8	2.4
		6	1.1	1.4
		7	0	1
		8	1.5	2.5
35	Untreated Proppant	6.5	5	

[0071] The oil absorption for each example was determined as was described above for the water absorption, wherein a tetradecane solution (obtained from Sigma-Aldrich) was used in place of the deionized water. The oil absorptions values (an average of 2 measurements) for Examples 1-8 are provided in Table 2, above.

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Comparative Example

[0072] The water absorption of a natural (standard Ottawa) sand (obtained from EM Science, Gibbstown, NJ) was measured as described above for Examples 1-8, and determined to be 19%. There was no contact angle that could be measured because the liquids were absorbed.

Example 9

[0073] A standard Ottawa sand (EM Science) was treated with a 10% by weight fluorochemical silane solution as described in Example 6. The weight percent of the active fluoropolymer added to the proppants was about 2% by weight. This treated proppant (sand) had a water absorption value of 1.7%. The water and oil contact angles of the treated proppant were 124 and 108, respectively.

Example 10

[0074] The standard Ottawa sand (EM Science) was treated with a fluorochemical silane as described in Example 3. This treated proppant (sand) had a water absorption value of 5%.

Example 11

[0075] A white resin coated ceramic proppant (obtained from BJ Services, Houston, TX under the trade designation "LITEPROPTM 175") was treated with a treatment solution as described in Example 4. The weight percent of the active fluoropolymer added to the proppants was about 2%.

Example 12

[0076] A white resin coated ceramic proppant ("LITEPROPTM 175") was treated with a treatment solution as described in Example 6. The weight percent of active fluoropolymer added to the proppants was about 2%.

Example 13

[0077] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 3. The weight percent of active silane added to the proppants was about 1%.

Example 14

[0078] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 3, except the treatment solution was prepared by diluting a fluorinated disilane (100% solids; obtained from 3M Company under the trade designation "3M EASY CLEAN COATING ECC-1000") to 5% using a fluorinated fluid (obtained from 3M Company under the trade designation "3M NOVEC ENGINEERED FLUID HFE-7100"), and then adding 1%, by weight, based on the total weight of the diluted solution, hydrochloric acid (37% by weight concentration). The weight percent of active silane added to the proppants was about 1%.

Example 15

[0079] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 5. The weight percent of active $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$ added to the proppants was 1%.

Example 16

[0080] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 5, except 1% by weight acid (37% by weight concentration) was added to the treatment solution. The weight percent of active $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$ added to the proppants was about 1%.

Example 17

[0081] Example 17 was prepared as described in Example 14, except that no hydrochloric acid was added to the treatment solution. The weight percent of active silane added to the proppants was about 1%.

5

Example 18

[0082] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 7. The weight percent of $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$ added to the proppants was about 1%.

10

Example 19

[0083] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 8. The weight percent of polymeric silane added to the proppants was about 1%.

15

Example 20

[0084] A white resin coated ceramic proppant ("LITEPROP 175") was treated with a treatment solution as described in Example 5, except the treatment solution was a 10% solution of fluorinated urethane silane (obtained from 3M Company under the trade designation "PM-490"), and about 20 grams of the treatment solution were added to about 100 grams of proppant.

20

[0085] The contact angles of the treated proppants of the Comparative Example and Examples 11-20 were measured as described above. The results are listed in Table 3, below.

25

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Table 3

	<u>Example</u>	<u>Static Water Contact Angle (degree)</u>	<u>Static Hexadecane Contact Angle (degree)</u>
5	11	126	107
	12	120	71
	13	115	94
	14	110	Absorbed
	15	116	115
10	16	114	110
	17	--	--
	18	115	104
	19	115	Absorbed
	20	118	118
15			

[0086] The water and oil absorption rate of Examples 11-20 (and the untreated white resin coated ceramic proppant ("LITEPROP 175")) were also determined as described above. These results are listed in Table 4, below.

20

Table 4

	<u>Example</u>	<u>Water Absorption (%)</u>	<u>Oil Absorption (%)</u>
	11	0.5	4
	12	8	10
25	13	0	11
	14	5	11
	15	0	5
	16	0.5	8
	17	7	9
30	18	0	8
	19	6	15
	20	4	10
35	Untreated ("LITEPROP 175") Proppant	25	20

[0087] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

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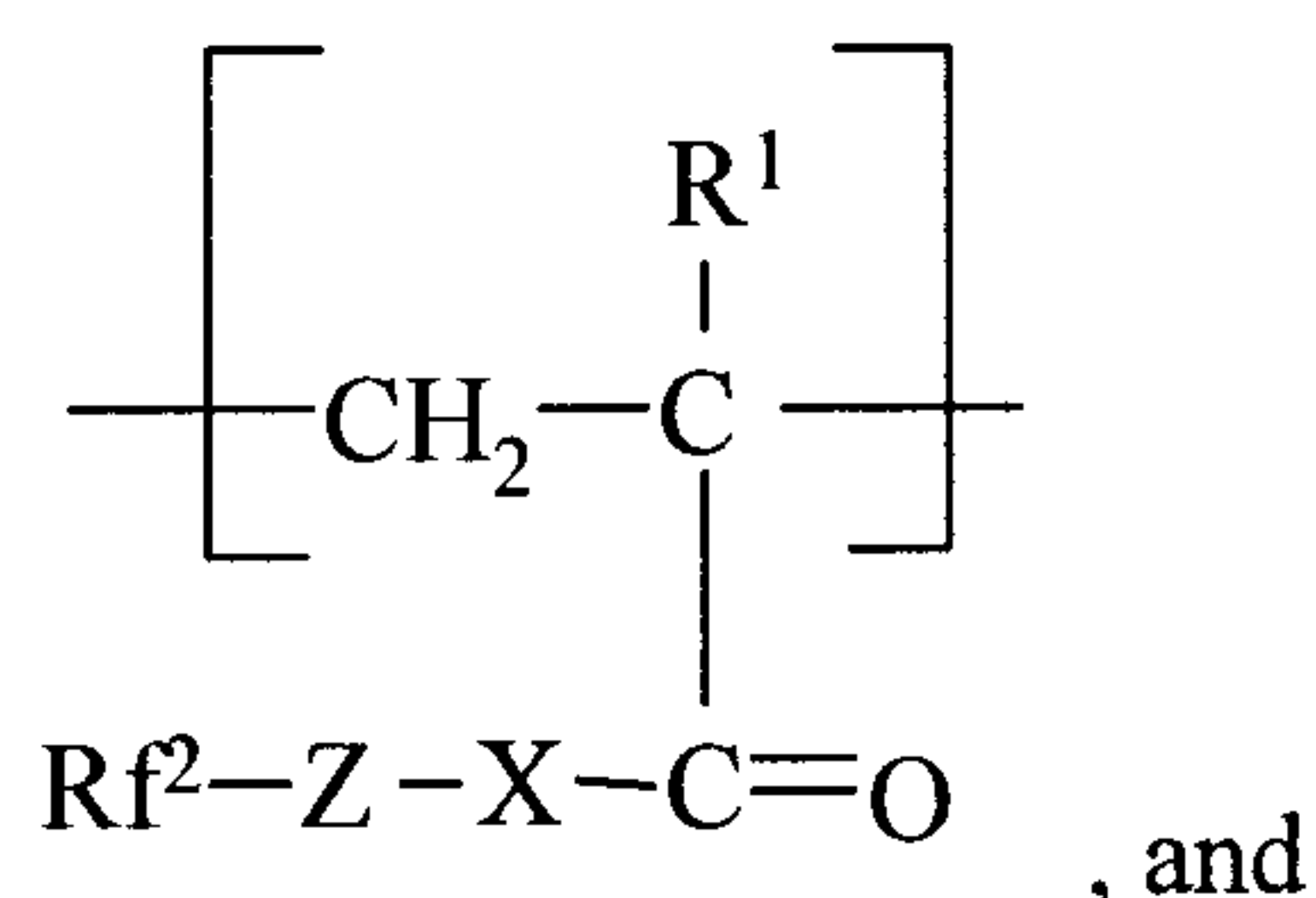
CLAIMS:

1. A particle treated with at least one fluorinated siloxane, the particle being at least 500 micrometers in size, wherein the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from:

5 $Rf\{-Q-[SiY_{3-x}(R)_x]_y\}_z$;

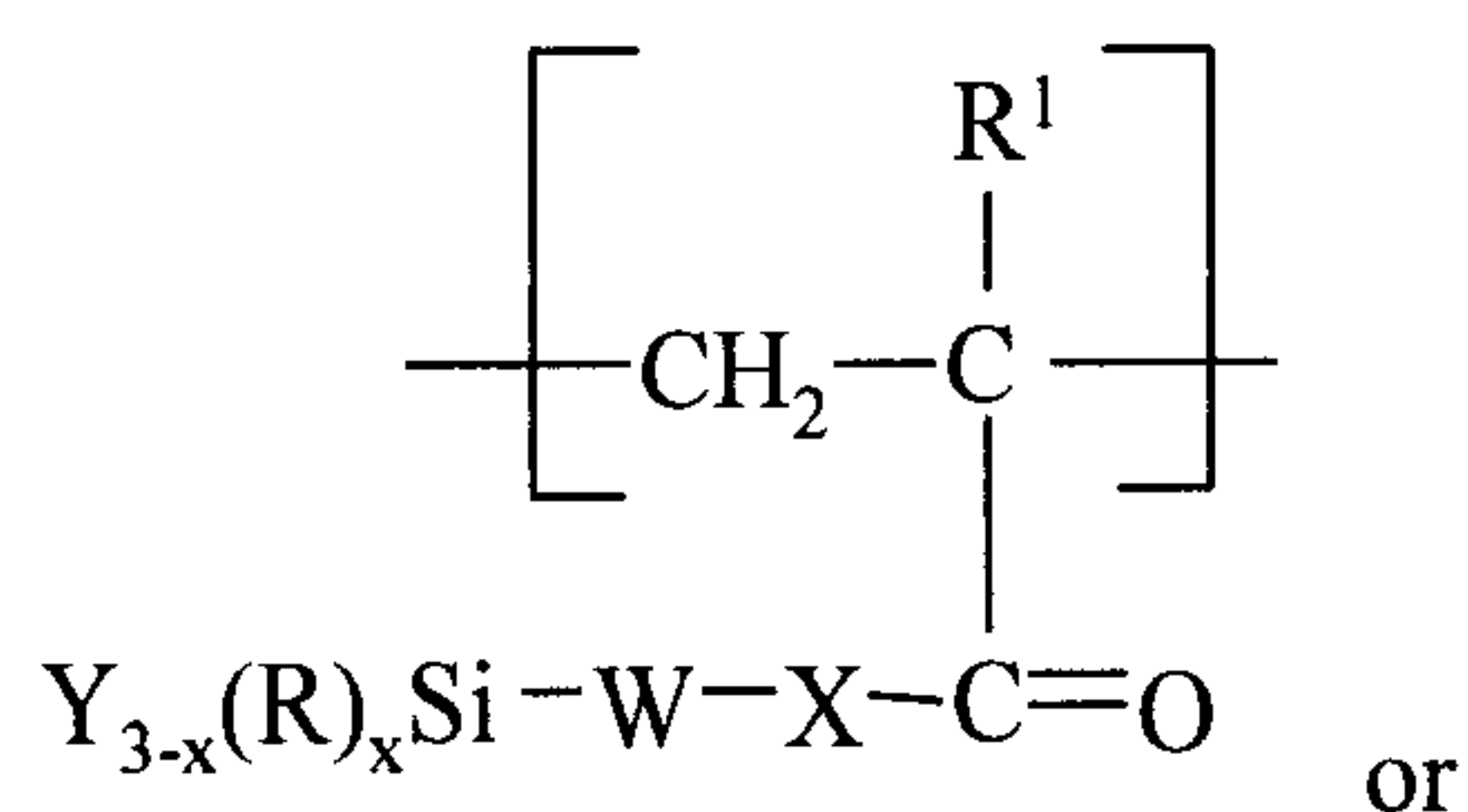
a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula:

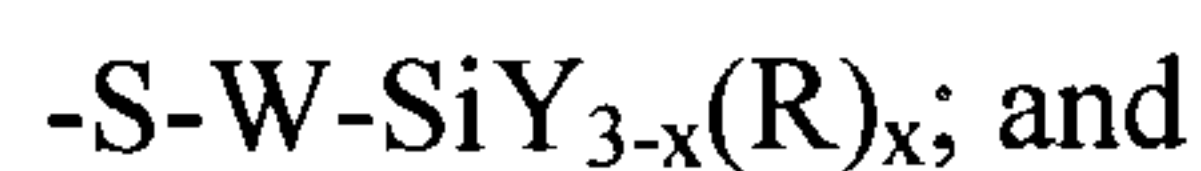


at least one of

10 at least one divalent unit represented by the formula:



a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

15 at least one end group represented by the formula ---O---Z---Rf^2 , and

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at least one end group represented by the formula $-X^1-W-SiY_{3-x}(R)_x$;

wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-;

5 Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

each R is independently alkyl having one to six carbon atoms or aryl;

10 Q is a divalent or trivalent hydrocarbon linking group having at least 2 and not more than 25 carbon atoms and containing from 1 to 4 functional groups selected from ester, amide, sulfonamide, carbonyl, carbonate, urea, and carbamate;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen;

each R¹ is independently hydrogen or alkyl having one to four carbon atoms;

each W is independently alkylene, arylalkylene, or arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

15 each X is independently -NH-, -O-, or -S-;

X¹ is -N(H)-, -S-, -O-, -O-C(O)-NH-, and -O-alkylene-O-C(O)-NH-;

Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

20 z is 1, 2, 3, or 4,

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wherein the particle is made of a material selected from sand, thermoplastic, clay, glass, and alumina.

2. The treated particle according to claim 1, wherein the fluorinated siloxane is bonded to the treated particle.

5 3. The treated particle according to claim 1 or 2, wherein the fluorinated siloxane comprises a condensation product of at least one fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-O-(CH_2)_nN(R^4)S(O)_2-Rf^3$,

and

10 at least one end group represented by the formula $-NH-(CH_2)_n-SiY_3$;

wherein

R^4 is alkyl having one to four carbon atoms;

Rf^3 is a perfluoroalkyl group having from one to eight carbon atoms;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen; and

15 each n is independently an integer from 1 to 4.

4. The treated particle according to any one of claims 1 to 3, wherein the treated particle has a plurality of pores, and wherein the treated particle has at least one of water or oil imbibition up to 95% as compared to a comparable, untreated particle.

5. A plurality of particles, wherein at least a portion are the treated particles
20 according to any one of claims 1 to 4.

6. A plurality of particles, wherein at least 50 percent by weight are the treated particles according to any one of claims 1 to 4.

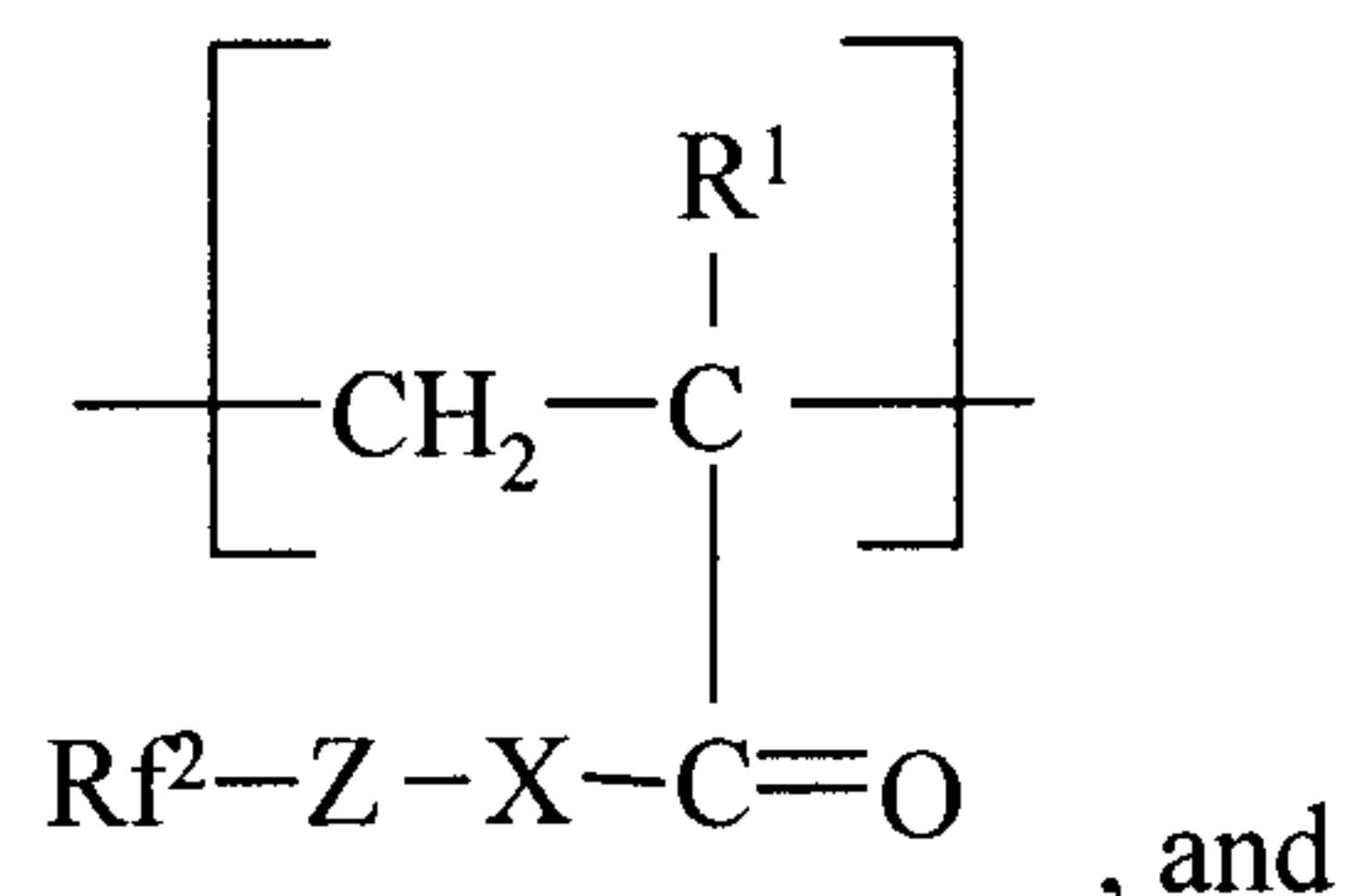
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7. A ceramic particle treated with at least one fluorinated siloxane, wherein the ceramic particle has a plurality of pores, wherein the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from:



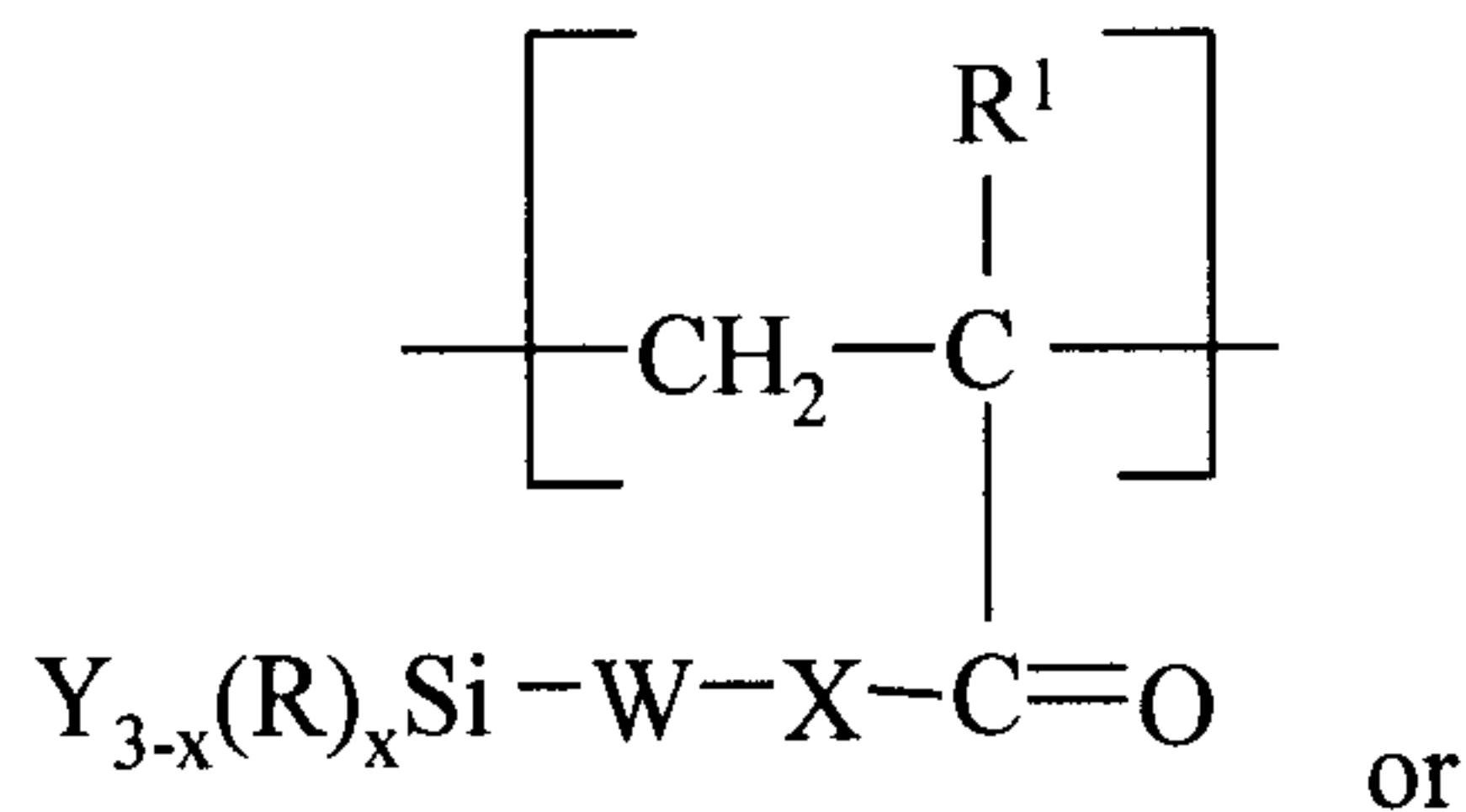
5 a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula:



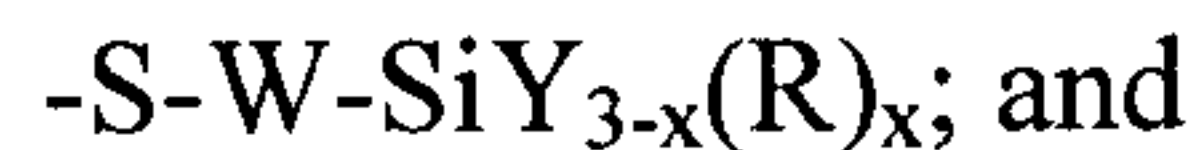
at least one of

at least one divalent unit represented by the formula:



10

a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

15

at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

wherein

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Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-;

Rf² is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

5 each R is independently alkyl having one to six carbon atoms or aryl;

Q is a divalent or trivalent hydrocarbon linking group having at least 2 and not more than 25 carbon atoms and containing from 1 to 4 functional groups selected from ester, amide, sulfonamide, carbonyl, carbonate, urea, and carbamate;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen;

10 each R¹ is independently hydrogen or alkyl having one to four carbon atoms;

each W is independently alkylene, arylalkylene, or arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently -NH-, -O-, or -S-;

X¹ is -N(H)-, -S-, -O-, -O-C(O)-NH-, or -O-alkylene-O-C(O)-NH-;

15 Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

z is 1, 2, 3, or 4.

8. The treated, ceramic particle according to claim 7 having a density of at
20 least 2 g/cm³.

9. The treated, ceramic particle according to claim 7 or 8, wherein the fluorinated siloxane is bonded to the treated particle.

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10. The treated, ceramic particle according to any one of claims 7 to 9, wherein the fluorinated siloxane comprises a condensation product of at least one fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-O-(CH_2)_nN(R^4)S(O)_2-Rf^3$,

5 and

at least one end group represented by the formula $-NH-(CH_2)_n-SiY_3$;

wherein

R^4 is alkyl having one to four carbon atoms;

Rf^3 is a perfluoroalkyl group having from one to eight carbon atoms;

10 each Y is independently hydroxyl, alkoxy, acyloxy, or halogen; and

each n is independently an integer from 1 to 4.

11. The treated, ceramic particle according to any one of claims 7 to 10, wherein the particle is made of a material selected from sand, clay, glass, and alumina.

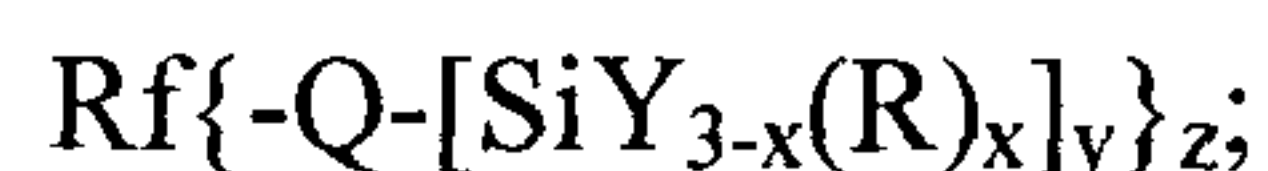
12. The treated, ceramic particle according to any one of claims 7 to 11, wherein
15 the treated particle has at least one of water or oil imbibition up to 95% as compared to a comparable, untreated particle.

13. A plurality of particles, wherein at least a portion are the treated, ceramic particles according to any one of claims 7 to 12.

14. A plurality of particles, wherein at least 50 percent by weight are the treated,
20 ceramic particles according to any one of claims 7 to 13.

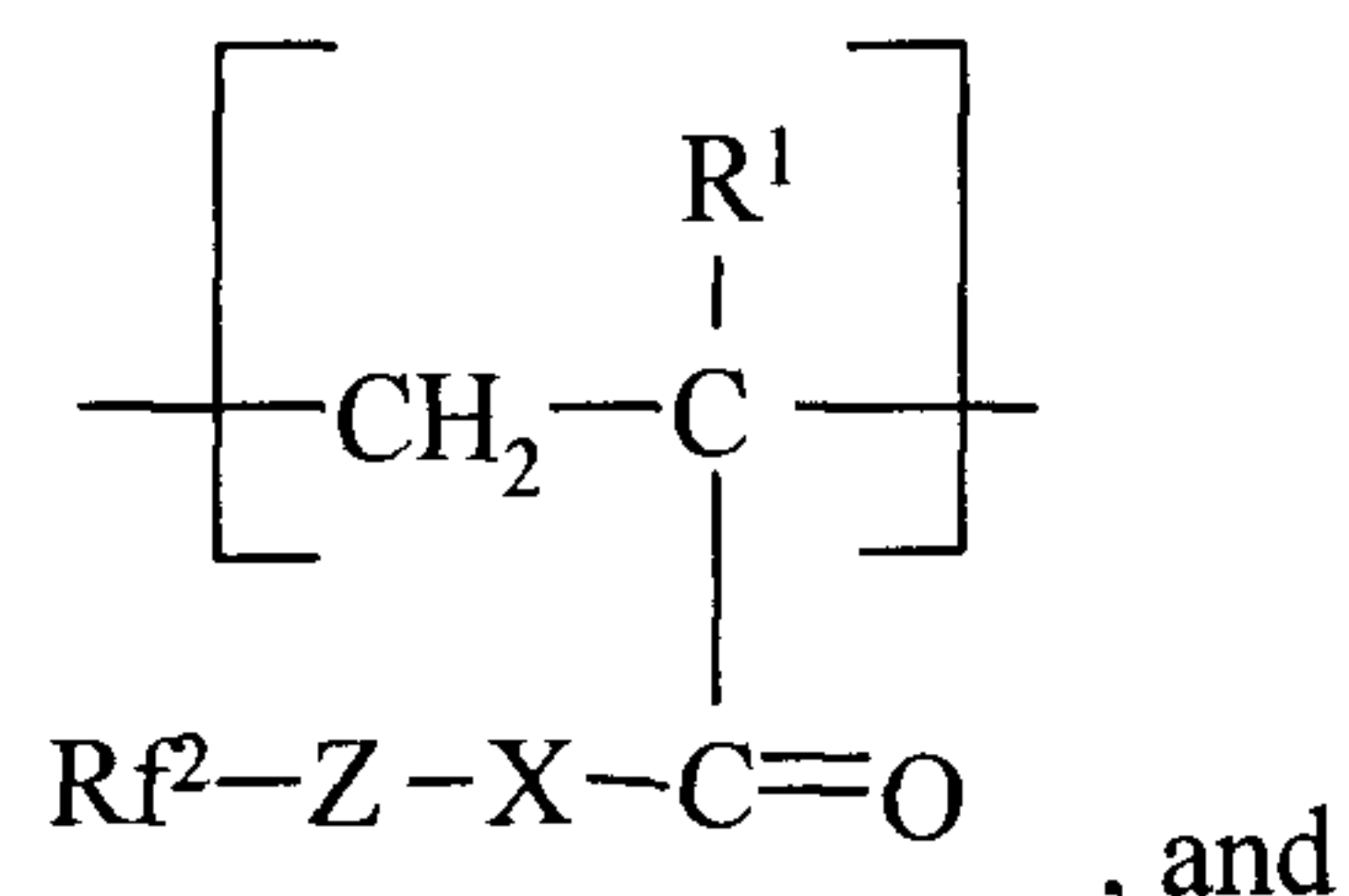
15. A man-made proppant treated with at least one fluorinated siloxane, wherein the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from:

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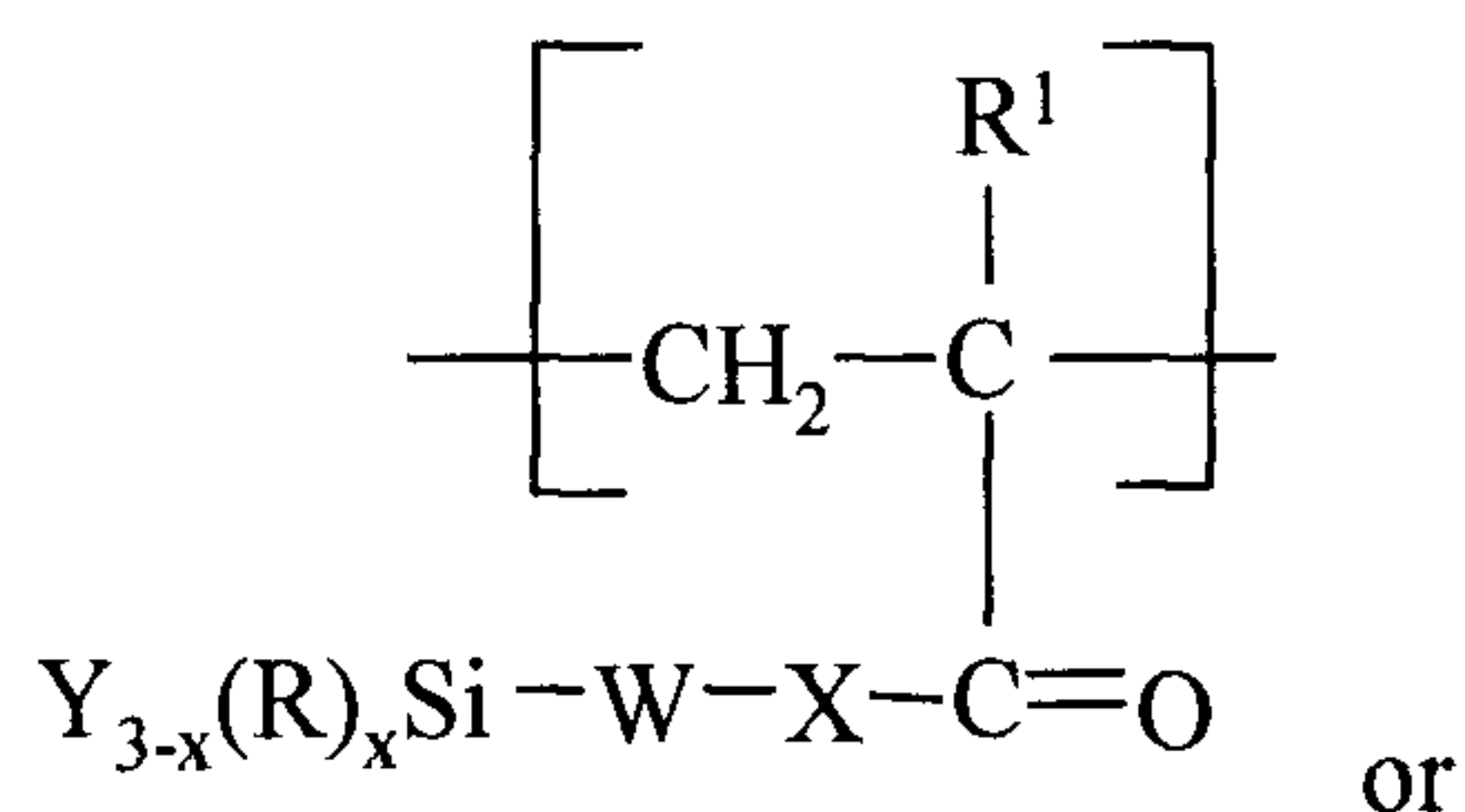
a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula:

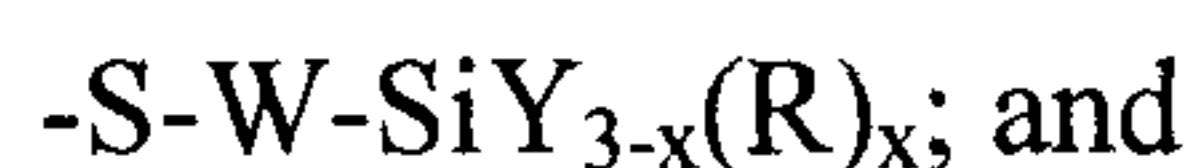


5 at least one of

at least one divalent unit represented by the formula:



a chain-terminating group represented by the formula:



10 a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

wherein

Rf is a monovalent or multivalent perfluoroalkyl group optionally interrupted

15 by at least one $-\text{O}-$;

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Rf^2 is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

each R is independently alkyl having one to six carbon atoms or aryl;

Q is a divalent or trivalent hydrocarbon linking group having at least 2 and not more than 25 carbon atoms and containing from 1 to 4 functional groups selected from ester, amide, sulfonamide, carbonyl, carbonate, urea, and carbamate;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen;

each R^1 is independently hydrogen or alkyl having one to four carbon atoms;

each W is independently alkylene, arylalkylene, or arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently -NH-, -O-, or -S-;

X^1 is -N(H)-, -S-, -O-, -O-C(O)-NH-, or -O-alkylene-O-C(O)-NH-;

Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

z is 1, 2, 3, or 4.

16. The treated, man-made proppant according to claim 15, wherein the fluorinated siloxane is bonded to the man-made proppant.

17. The treated, man-made proppant according to claims 15 or 16, wherein the fluorinated siloxane comprises the condensation product of at least one fluorinated urethane oligomer of at least two repeat units comprising:

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at least one end group represented by the formula $-\text{O}-(\text{CH}_2)_n\text{N}(\text{R}^4)\text{S}(\text{O})_2\text{Rf}^3$,

and

at least one end group represented by the formula $-\text{NH}-(\text{CH}_2)_n\text{SiY}_3$;

wherein

5

R^4 is alkyl having one to four carbon atoms;

Rf^3 is a perfluoroalkyl group having from one to eight carbon atoms;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen; and

each n is independently an integer from 1 to 4.

18. The treated, man-made proppant according to any one of claims 15 to 17,
10 wherein the man-made proppant is made of a material selected from sand, thermoplastic, clay, glass, and alumina.

19. The treated, man-made proppant according to any one of claims 15 to 18,
wherein the treated, man-made proppant has a plurality of pores, and wherein the treated,
man-made proppant has at least one of water or oil imbibition up to 95% as compared to a
15 comparable, untreated proppant.

20. A plurality of the treated, man-made proppants according to any one of claims 15 to 19.

21. A method of fracturing a subterranean geological formation comprising hydrocarbons, the method comprising:

20 injecting a hydraulic fluid into a subterranean geological formation comprising hydrocarbons at a rate and pressure sufficient to open a fracture therein; and

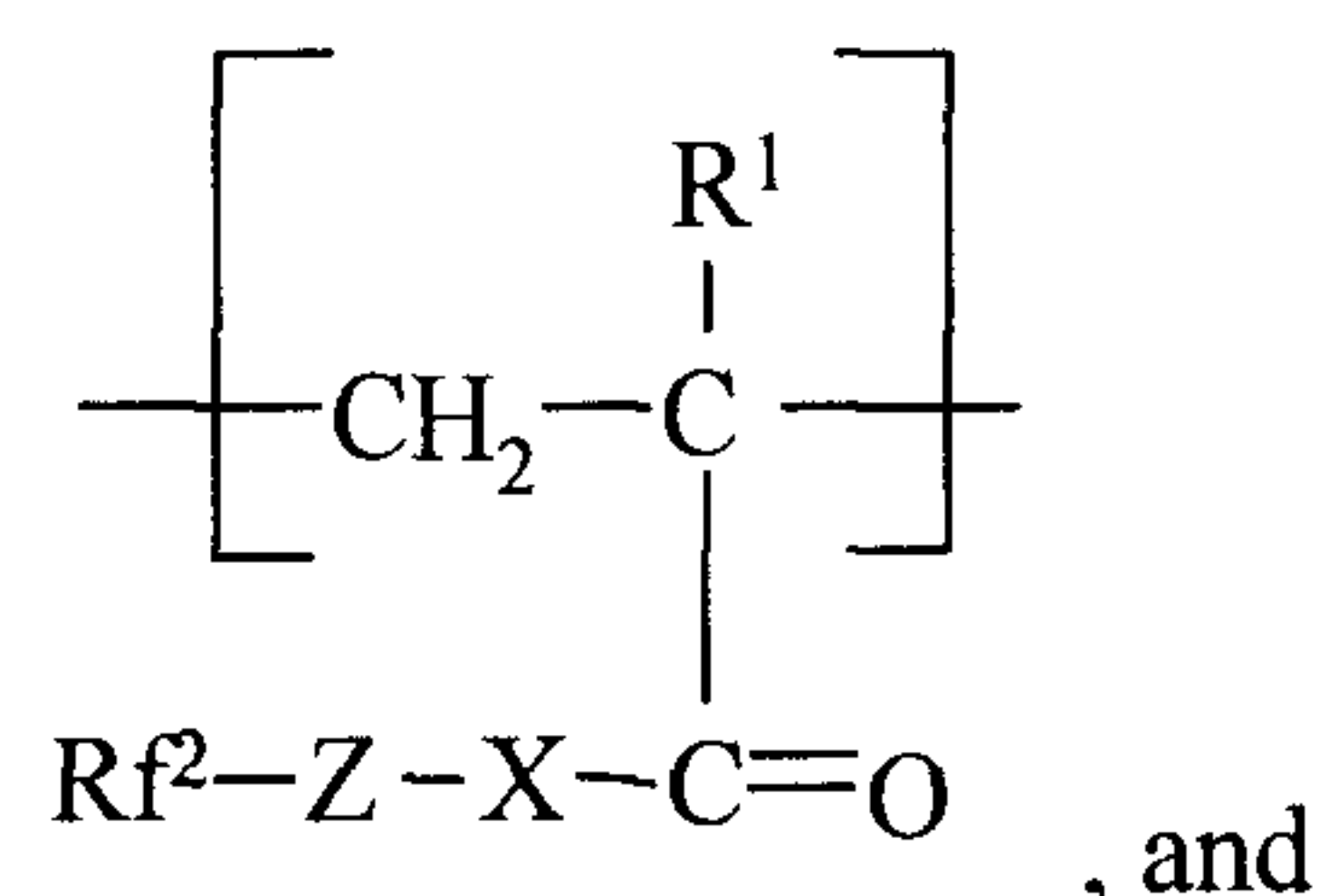
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injecting into the fracture a fluid comprising a plurality of particles treated with at least one fluorinated siloxane, wherein the fluorinated siloxane comprises a condensation product of at least one reactive fluorinated silane selected from:



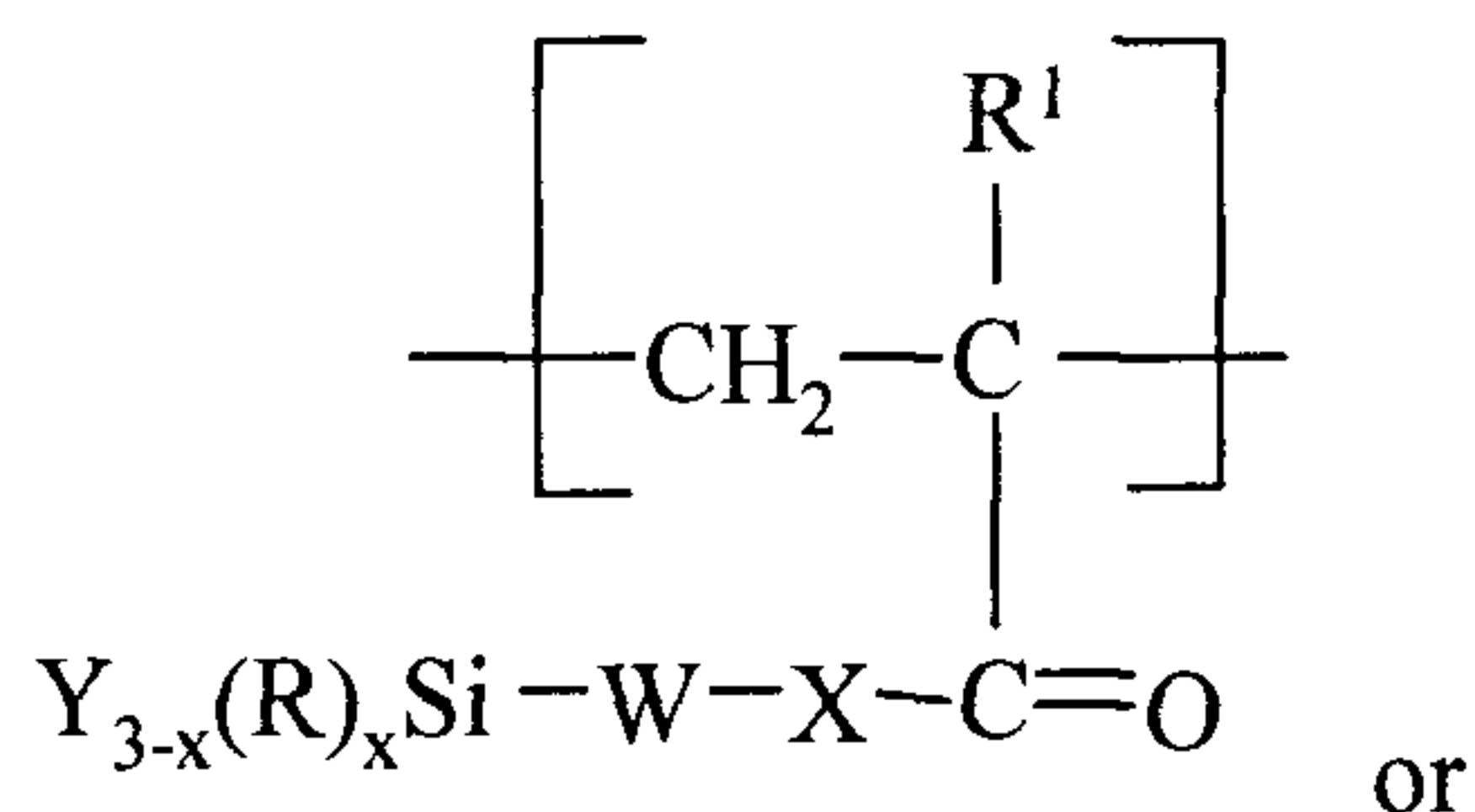
5 a polymeric fluorinated composition comprising:

at least one divalent unit represented by the formula:



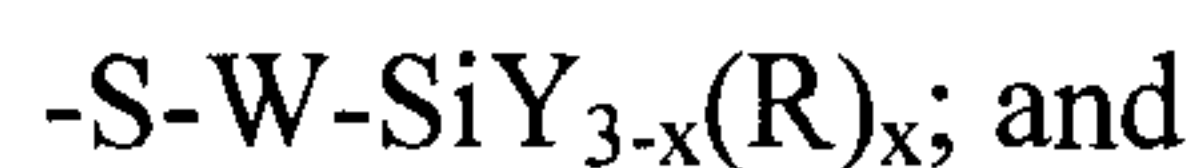
at least one of

at least one divalent unit represented by the formula:



10

a chain-terminating group represented by the formula:



a fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-\text{O}-\text{Z}-\text{Rf}^2$, and

15

at least one end group represented by the formula $-\text{X}^1-\text{W}-\text{SiY}_{3-x}(\text{R})_x$;

wherein

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R_f is a monovalent or multivalent perfluoroalkyl group optionally interrupted by at least one -O-;

R_f² is a monovalent perfluoroalkyl group optionally interrupted by at least one -O-;

5 each R is independently alkyl having one to six carbon atoms or aryl;

Q is a divalent or trivalent hydrocarbon linking group having at least 2 and not more than 25 carbon atoms and containing from 1 to 4 functional groups selected from ester, amide, sulfonamide, carbonyl, carbonate, urea, and carbamate;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen;

10 each R¹ is independently hydrogen or alkyl having one to four carbon atoms;

each W is independently alkylene, arylalkylene, or arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom;

each X is independently -NH-, -O-, or -S-;

X¹ is -N(H)-, -S-, -O-, -O-C(O)-NH-, or -O-alkylene-O-C(O)-NH-;

15 Z is a divalent organic linking group;

x is 0, 1, or 2;

y is 1 or 2; and

z is 1, 2, 3, or 4.

22. The method according to claim 21, wherein the particles are made of a material
20 selected from sand, thermoplastic, clay, glass, or alumina.

23. The method according to claim 21 or 22, wherein the particles are man-made proppants.

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24. The method according to any one of claims 21 to 23, wherein the particles are at least 500 micrometers in size.

25. The method according to any one of claims 21 to 24, wherein the fluorinated siloxane comprises a condensation product of at least one fluorinated urethane oligomer of at least two repeat units comprising:

at least one end group represented by the formula $-O-(CH_2)_nN(R^4)S(O)_2-Rf^3$,

and

at least one end group represented by the formula $-NH-(CH_2)_n-Si[Y_3]$;

wherein

10 R^4 is alkyl having one to four carbon atoms;

Rf^3 is a perfluoroalkyl group having from one to eight carbon atoms;

each Y is independently hydroxyl, alkoxy, acyloxy, or halogen; and

each n is independently an integer from 1 to 4.

26. The method according to any one of claims 21 to 25, wherein the fluorinated siloxane is bonded to the particles.

27. The method according to any one of claims 21 to 26, wherein the particles are treated with at least one precursor of the fluorinated siloxane prior to injection into the fracture.

28. The method according to any one of claims 21 to 27, wherein the particles are treated with at least one precursor of the fluorinated siloxane during injection into the fracture.

29. The method according to any one of claims 21 to 28, wherein the fracture has a conductivity improved by the presence of the fluorinated siloxane.